CHARACTERISING NATURAL ORGANIC MATTER IN SURFACE WATERS AND THE MINIMISATION OF DISINFECTION BY-PRODUCT FORMATION

By

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Abstract

Modern water treatment processes are necessary to create an adequate and continuous supply of water that meets regulatory standards. The presence of natural organic matter (NOM) in water courses impacts negatively upon aesthetic and chemical standards and as such requires removal during water treatment processes. Variable structural composition and sources of NOM denote that high NOM removal efficiencies are rarely achieved at conventional water treatment works (WTW). Poor removal of NOM can result in biofilm re-growth in distribution systems and the formation of potentially carcinogenic disinfectant by-products (DBP) such as trihalomethanes (THM) and haloacetic acids (HAA), formed when residual NOM reacts with disinfectants such as chlorine.

NOM characterisation methods were used to investigate NOM composition at sixteen surface water sites operated by Severn Trent Water Ltd, to establish potential links between NOM character and the formation of potential carcinogeous DBP, and assess potential DOC removal using current and low pH coagulation. Comparisons were made between existing NOM characterisation methods and the identification of limitations. HPSEC and fluorescence EEM spectroscopy were found to be reliable and practical measures of NOM character and treatability. Statistical analysis techniques such as discriminant analysis and principal component analysis proved essential analysis tools for large data sets, identifying sites with similar raw characteristics and highlighted relationships with DBP precursors.

The suitability of carbon isotopes analysis and environmental nanoparticles analysis as two novel NOM characterisation methods were also investigated and compared with existing methods. Carbon isotope analysis documented an input of heavier ^{13}C signatures and a decreased percentage modern carbon ^{14}C. Possible causes for this were the addition of GAC fines, fractionation of $^{12/13}C$ through treatment processes or through microbial growth on the GAC column. Finally, a detailed assessment of current coagulation potential for increased NOM removal and the potential for a reduction in DBP formation during differing NOM composition profiles was investigated with an economic assessment for a river abstraction WTW with rapidly changing NOM character. Low pH coagulation was found to substantially increase potential DOC removal and limit THM, TTHMFP and HAAFP formation and identified the need for process optimisation on WTW before treatment alternatives are considered.

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Abbreviations

AFM	Atomic Force Microscopy
Al_{2+}	Aluminium sulphate
AU	Absorbance Units
AWWARF	American Water Works Association Research Foundation
BrdiCl	Bromodichloride
Brmfrm	Bromoform
Chlrfm	Chloroform
CldiBr	Chlorodibromide
ClO_2	Chloride dioxide
CO_2	Carbon dioxide
Da	Daltons
DAF	Dissolved Air Flotation
DBP	Disinfection By-Product
D_H	Hydrodynamic diameter
DI	De-Ionised
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DWI	Drinking Water Inspectorate
D_Z	Difference coefficient
ECD	Electron Capture Detector
EEM	Excitation Emission Matrix

EU	European Union
FA	Fulvic Acid
FAF	Fulvic Acid Fraction
FBC	Flat Bottomed Clarifier
FENAC	Facility for Environmental Nanoparticle Analysis and Characterisation
$FeSO_4$	Ferric Sulphate
FIFFF	Field Flow Fractionation
FT-IR	Fourier Transform Infrared
GAC	Granular Activated Carbon
GC-MS	Gas Chromatography Mass Spectroscopy
HA	Humic Acid
HAA	Haloacetic Acid
HAAFP	Haloacetic Acid Formation Potential
HAF	Humic Acid Fraction
HAN	Haloacetic Nitriles
HBC	Hopper Bottomed Clarifiers
HCl	Hydrochloric acid
HPI	Hydrophilic
HPIA	Hydrophilic Acid
HPINA	Hydrophilic Non Acid
HPLC	High Performance Liquid Chromatography
HPO	Hydrophobic
HPLC	High Performance Liquid Chromatography
HPSEC	High Performance Size Exclusion Chromatography

ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IEP	Iso-Electric Point
IWA	International Water Association
KOH	Potassium hydroxide
M	Molar
MCL	Maximum Contaminant Level
MIEX®	Magnetic Ion Exchange Resin
Ml	Megalitres
MW	Molecular Weight
NaOH	Sodium Hydroxide
NCI	National Cancer Institute
NERC	Natural Environment Research Council
NDMA	Nitrosodimethylamine
nm	Nano Meters
NRCF(E)	Natural Environment Research Council, Radiocarbon Facility
NMR	Nuclear Magnetic Resonance
NOM	Natural Organic Matter
NTA	Nanoparticle Tracking Analysis
NTU	Nephelometric Turbidity Units
ORS	Octopole Reaction System
PAC	Powdered Activated Carbon
PAFSiC	Powdered Activated Ferric-Silicate Chloride
PET	Polyethylene Terephthalate
RO	Reverse Osmosis

RPM	Revolutions Per Minute
s.d	Standard Deviation
STL	Severn Trent Laboratories
STW	Severn Trent Water
SUVA	Specific Ultraviolet Absorbance
TEM	Transmission Electron Microscopy
THM	Trihalomethane
THMFP	Trihalomethane Formation Potential
TTHM	Total Trihalomethane
TOC	Total Organic Carbon
UF	Ultra Filtration
UK	United Kingdom
UoB	University of Birmingham
USEPA	United States Environmental Protection Agency
UV_{254}	Ultraviolet Absorbance at 254 nm
VPDB	Vienna Pee Dee Beelemnite
WHO	World Heath Organisation
WTW	Water Treatment Works
µm	Micrometres

Chapter 1. Introduction

1.1 General

Natural Organic Matter (NOM) is present in natural waters throughout the world due to interactions between the hydrological cycle and both the biosphere and geosphere (Frimmel, 1998). NOM varies spatially and temporally and its character is dependent on the surrounding environment and source material and the interactions between them, producing variations in acidity, molecular weight and charge density.

Aesthetically NOM is a source of colour in natural waters and must be minimised in order to comply with current DWI Water Quality standards derived from European law (DWI, 2010). Traditionally, treatment with trivalent coagulants coupled with flocculation has proved a successful strategy to aid NOM removal through clarification. Coagulation/flocculation of colloidal material is driven by charge neutralization and charge complexation/precipitation for soluble compounds, with additional removal occurring due to adsorption on to precipitated flocs and metal hydroxides (Randtke, 1988).

In recent years, operational difficulties at water treatment works (WTW) consistently focus on the removal of large quantities of NOM in times of heavy rainfall or snowmelt with incomplete removal of NOM causing problems through the subsequent treatment processes (Sharp et al., 2004). In coagulation NOM coatings tend to dominate the properties of inorganic colloids (Wilkinson et al., 1997b) reducing particle collision efficiency, resulting in the formation of more fragile flocs which are more susceptible to shear stresses (Bache et

al., 1997, Jarvis et al., 2005a). Diminished removal rates of NOM increase particle loads on filters, reducing filter run lifetimes and increasing the need for more frequent filter backwashing (Jarvis et al., 2008). Reactions between NOM and chemical disinfectants such as chlorine and chloramines lead to the formation of disinfection by-products (DBP) such as haloacetic acids (HAA) and trihalomethanes (THM), which have been identified as potential carcinogens (Hrudey, 2009, Baytak et al., 2008, Nieuwenhuijsen et al., 2009).

Current drinking water regulations indicate maximum contaminant level (MCL) values of 100 μgL^{-1} for THM for UK drinking water. Although HAA are currently unregulated, it is anticipated a HAA or other DBP regulation will be introduced (DEFRA/DWI, 2008, Bond et al., 2010). The US Environmental Protection Agency (EPA) regulates THM at 80 μgL^{-1} and HAA_5 at 60 μgL^{-1}. Water utilities are therefore being placed under increasing pressure to maximise NOM removal and limit the amount of DBP at consumer tap.

With seasonality influences and complex composition dependant on catchment characteristics, there are an undeterminable number of factors influencing NOM composition which ultimately results in WTW unable to predetermine variations in NOM composition and tailor treatment accordingly. Owing to an inability to predict variations in NOM on a local scale, methods for NOM characterisation are of intrinsic value for modern water treatment.

1.2 Scope of study

In the work presented in this thesis, various NOM characterisation methods were used to quantitatively and qualitatively assess the NOM over a broad range of catchments operated by Severn Trent Water (STW). NOM characterisation can provide an insight into the efficiency of conventional treatment methods and the formation of potential DBP. The purpose of this thesis was therefore to investigate the character of NOM at sixteen surface WTW in Midlands region of the UK using existing and new technologies, critically analyse these new and existing characterisation technologies, investigate links between NOM characteristics and DBP formation and identify strategies for increased NOM removal through conventional treatment. The specific objectives were:

(i) To evaluate the use of existing characterisation methods for the investigation of NOM composition and in the identification of key trends in NOM character, existing and achievable removal and DBP formation.

(ii) To investigate the potential for carbon isotopic analysis and environmental colloidal analysis as NOM characterisation tools, to address current characterisation needs and to identify trends with DBP formation.

(iii) To establish whether current treatment conditions are capable of removing increased amounts of NOM in order to reduce DBP formation.

1.3 Thesis organisation

This thesis builds on previous research into the characterisation of NOM at surface water treatment sites and the management of THM in distribution systems completed at the University of Birmingham (UoB) in conjunction with Severn Trent Water (STW) (Bieroza et al., 2009a, Bieroza, 2009, Bieroza et al., 2009b, Brown, 2009, Brown et al., 2010). Supplementary data used in chapter 4 and 5 was provided by Severn Trent Water Ltd.

Unless otherwise stated, all analyses were carried out by the author and all investigations were planned, collected and the majority of experimental work performed by the author and in collaboration with STW and UoB staff. Severn Trent Laboratories (STL) performed DOC, THM and THMFP sample analysis shown in Chapters 4, 5, 6 and 9. HPSEC and HAAFP sample analysis was sub-contracted to Cranfield University.

1.4 Structure of thesis

The subsequent chapters of the thesis are presented in the following way:

Chapter 2 – Literature review: This chapter presents a critical review of the existing literature on NOM, characterisation and removal, and includes analysis of potential tools for NOM characterisation. This chapter also focuses on the formation of DBP and removal strategies. The knowledge gap is defined alongside the justifications for the thesis.

Chapter 3 – Materials and methods: This chapter determines the terminology and components of experimental procedures used in this thesis at the UoB and STW laboratories, and additional analysis performed by STL and Cranfield University. A brief summary of the STW region and the study sites is then presented.

Chapter 4 – NOM characterisation of surface waters: The results and analysis of NOM characterisation at all the surface water sites, using existing NOM characterisation techniques are presented. The performance of existing coagulation methods are then analysed and the potential for increased removal and THM and HAA formation examined.

Chapter 5 – Relating organic matter characterisation to DBP formation using data mining: This chapter presents the results and analysis for the statistical analysis of NOM characterisation and THM and HAA formation potential. Principal component analysis and discriminant analysis methods are employed to determine potential relationships.

Chapter 6 – DBP precursor removal through low pH coagulation: This chapter utilises the characterisation studies of Chapters 4 and 5, and presents results and analysis of low pH coagulation experiments designed for the optimal removal of THM and HAA precursors over the summer and autumn periods of 2008. Estimates of costs for low pH coagulation are also presented.

Chapter 7 – Carbon isotopic analysis of surface water: The uses of carbon isotopes for NOM characterisation of surface water are considered. Results and analysis of carbon isotopes

through reservoir storage are also considered, and potential links between THM and carbon isotopes are investigated.

Chapter 8 – Carbon isotopic analysis through the water treatment process: This chapter is an investigation into the cause of isotopically heavy ^{13}C signatures and decreased percentage modern ^{14}C in post-GAC waters. Results and analysis are presented for carbon isotope analysis through the water treatment process at two contrasting surface water sites.

Chapter 9 – Analysis of colloidal material through a water treatment works: The results and analysis are presented for the utilisation of state-of-the-art environmental colloidal analysis techniques for NOM characterisation at five contrasting water treatment sites. The impact of water treatment on environmental colloids is also considered, as are potential links with THM and HAA formation.

Chapter 10 – Discussion: This chapter links together the research undertaken in the thesis with current knowledge and research trends.

Chapter 11 – Conclusions and future work recommendations: This chapter draws together the conclusions from the investigational chapters in relation to the thesis aims, and recommendations for future research are made.

1.5 Publications

The novelty of this work has led to the publication of a paper in a peer-reviewed journal, and the presentation of three papers and one poster at national and international conferences. Details are as follows;

Publications

Roe, J., Baker, A., Bridgeman, J., Relating organic matter character to trihalomentanes formation potential; a data mining approach. *Water Science and Technology; Water Supply*. 2008, 8, 6, 717 – 723.

Conferences

5th IWA International Young Water Professionals Conference, July 2010 – Platform presentation titled '*Carbon isotopic analysis of potential organic carbon inputs during the water treatment process*'.

5th IWA International Young Water Professionals Conference, July 2010 – Poster presentation titled '*Characterisation of environmental colloids through drinking water treatment in relation to disinfectant by product formation'*. Achieved first place in poster presentation competition.

3rd Developments in Water Treatment and Supply Conference, June 2009 – Platform presentation titled '*Carbon isotope analysis of freshwater and post-GAC dissolved organic matter*'.

1st Natural Organic Matter Conference; From Source to Tap, September 2008 – Platform presentation titled – '*Relating organic matter character to THM formation: A data mining approach*'.

Chapter 2. Literature Review

This chapter presents a critical review of the existing literature on NOM composition, characterisation and removal, linking it to the impact of NOM on water treatment and the formation of DBP. This chapter also discusses the existing and potential tools for NOM characterisation and then focuses on the removal of NOM in conventional water treatment processes and methods available for process optimisation or additional removal. The knowledge gap is then defined alongside the justifications for the thesis.

2.1 Natural organic matter, characterisation and removal

Modern water treatment processes are utilised in order to create an adequate and continuous supply of water that is chemically, bacteriologically and aesthetically pleasing (Gray, 2005). A major challenge in water treatment is the efficient removal of NOM with typical removal efficiencies varying from 20-90%; (Sharp et al., 2006c). Poor removal can lead to NOM reacting with disinfectants to form potential carcinogens DBP such as THM and HAA (Fabris et al., 2008). Additionally, the presence of NOM post treatment can aid biofilm re-growth in distribution networks, leading to further potential health risks (Egeberg and Alberts, 2002). Therefore, one of the principal aims of drinking water treatment is the optimisation of NOM removal.

2.1.1 NOM composition

NOM is a complex mixture of pedogenic (soil derived) and anthropogenic (water column) material derived from the contact of water with dead and living organic matter in the hydrological cycle (Kitis et al., 2002, Egeberg and Alberts, 2002). NOM is spatially and temporally variable and its abundance in natural aquatic environments provides a source of one of the largest active organic carbon reservoirs in the biosphere (McDonald et al., 2004, Battin et al., 2009), a quantity equal to the CO_2 content in the atmosphere (Cooper et al., 2008). NOM is present in dissolved, particulate and colloidal forms, and has a number of functions in aquatic systems. These include a carbon source for metabolism of living things, ecological and geochemical functions such as proton binding, influencing biogeochemical processes and photochemical reactions, transportation of inorganic and organic substrates and aggregation and photochemical reactivity (Frimmel, 1998, Xiaoying, 2001, Egeberg and Alberts, 2002, Gjessing et al., 1999, Maurice et al., 2002). Studies in organic matter characterisation have identified its main components as carbohydrates, lipids, protein polymers, humic macromolecules, nucleic acids and phenolic compounds (Edzwald, 1993, Wu et al., 2003). However, as NOM is highly source dependant only 25% of organic material (OM) is well characterised (Thomas, 1997).

The components of NOM are traceable to one of two sources within a catchment; autochthonous (within a water body) or allochthonous (within a soil profile) (Peschel and Wildt, 1988). Autochthonous NOM is predominantly produced within the water body itself by algae, bacteria and aquatic plants (Boyer et al., 2008). Photodegradation of NOM is also a considerable producer of autochthonous NOM in surface waters. Photochemical

"weathering" of originally allochthonous organic material can significantly influence the chemical character of OM, resulting in autochthonous by-products (Cory et al., 2007). Catchment based processes such as freezing/thawing and dehydration/rehydration are additional sources of autochthonous OM. Autochthonous NOM is predominantly phenolic and carboxylic in nature, containing amino acids, hydrocarbons, carbohydrates, sterols and low molecular acids (Fabris et al., 2008). NOM derived from these sources is typically enriched in aliphatic carbon and organic nitrogen (Boyer et al., 2008), absorbs less UV light and has fewer aromatic residues (Gondar et al., 2008). Qualities such as these cause autochthonous NOM typically to contain a smaller proportion of fluorophores (the fluorescent absorbing component of a particle) which are less recognisable with current characterisation techniques.

Allochthonous NOM is a mixture of acidic organic compounds of medium to high molecular weight, originating from the leaching of decaying terrestrial plant and animal material in a catchment (Tipping et al., 1999). Humic substances, consisting of humic, fulvic and hydrophilic acids dominate the composition of allochthonous NOM in UK surface water catchments and are characterised by high aromatic carbon content and low nitrogen content (Boyer et al., 2008). Recent estimations approximate the quantity of humic substances in natural waters to be 50-75% of DOC (McDonald et al., 2004, Scott et al., 2001, Kim and Yu, 2005), although observed upward trends of DOC in surface waters could further increase this dominance in future (Evans et al., 2006, Chapman et al., 2008, Tipping et al., 1999, Tipping et al., 2007). With such a diverse mixture of material in catchments, humic substances can vary greatly in size and aromaticity, but can be further distinguished by their hydrophobic (HPO) and hydrophilic (HPI) properties.

HPO organics typically consist of humic and fulvic acids, which exert a significantly higher charge density than the HPI fraction and are responsible for the yellow/orange colourings of water (Sharp et al., 2006a, Gregor et al., 1997). Fulvic acids comprise polycarboxylates of various degrees of aromaticity and molecular mass, their abundance in DOC makes fulvic material the largest source of mobile organic carbon on the earth (Sharp et al., 2006a, Reemtsma et al., 2008). Fulvic acid molecular weights range from 600-1000 Da, are soluble under all pH ranges and typically impose a strong negative surface charge in raw water profiles (McDonald et al., 2004, Sharp et al., 2006b). Humic substances, although contributing to a lesser extent to total DOC, are larger particles with higher molecular weights of 1500-5000 Da (McDonald et al., 2004). Humic acids have a larger charge density than fulvic acids, ranging between 5-10 meq g^{-1} (Sharp et al., 2006b, Sutton and Sposito, 2005). Reduced biodegradability increases the likelihood of accumulation in surface waters over the short term (Sutton and Sposito, 2005). Properties such as size and increased surface charge respond positively to existing removal techniques for example, coagulation with hydrolysed metal salts. Their complex properties still make humic and fulvic acids among the least characterised components in the environment (Lead and Wilkinson, 2006). Humic and fulvic-like material can be fractionated into their different components using techniques such as resin extraction and fluorescence. HPI organics comparatively are smaller, colourless and have little or no charge density, which is intensified in waters with low turbidity (Bolto et al., 2002). Such qualities make the removal of the HPI organic fraction one of the greatest challenges to modern water treatment.

2.1.2 Factors affecting NOM composition

The composition of NOM is highly dependent on formation conditions, most notably the catchment basin (Sharp et al., 2006d). Hydrological pathways, temperature and sunlight and biological predominance help determine relative compositions of NOM in surface waters. Typically, upland and densely vegetated catchments with a higher percentage peat cover have a higher incidence of humic and fulvic-like material. This results in increasingly coloured and turbid water and is also observed in agricultural catchments where the total soil carbon source has been disturbed. Lowland catchments will have greater levels of HPI acids and neutrals due to non-irrigated arable land use and additional urban areas (Bieroza et al., 2009b). Additionally, as NOM is transported through catchments its composition will be altered by continuous metabolism and photodegradation through fluvial networks. Battin et al., (2009) concludes that downstream ecosystems are a legacy of prior metabolic activities from upstream sources.

Recent research into the influences of NOM composition and character have focused on the seasonal changes experienced in UK source waters as THM formation is shown to be more prevalent in summer months due to increased temperatures (Goslan et al., 2002). In 2001, Scott et al., published data on a four year study into seasonal variation in NOM. This concluded that a 20-80% increase in the HPI content in source waters can be observed in summer months. A catchment dependent NOM composition however means that such high variation may not be evident in all catchments. Sharp et al. (2006e) also reported increase in the HPI content of DOC at UK moorland sites however average increases were significantly lower than those reported by Scott et al., (2001) at 25-41%. Explanations for

this point to field manipulation experiments conducted by Tipping et al., (1999), which published data confirming that higher average temperatures in summer months resulted in greater warming and drying of soils, accelerating the production of NOM through increased microbial activity. This, combined with limited rainfall and soil water movement restrict the release of DOM until the heavy rainfall of late summer and early autumn (Scott et al., 2001). In any one storm event, 50% of the total NOM can be transported into the system in the first 10% of the total duration (Clark et al., 2007). DOC concentrations then have a tendency to fall due to the exhaustion of DOC supply (Tipping et al., 2009). NOM is transported to surface waters by surface run-off and near surface lateral flow, and can increase DOC concentrations by up to 40% (Hurst et al., 2004). HPI material is leached quicker due to its ease of dissolution whereas HPO fulvic acids are released more gradually.

Studies have indicated seasonality of NOM is more prevalent at sites of increased HPO content (Roe et al., 2008), which are in agreement with research by Tipping et al., (1999) which states that upland sources experience greater variations in NOM profiles during seasonal changes (Tipping et al., 1999). Investigations into the release of DOM in differing soil types reported that peaty soils export substantially greater amounts of DOC than other soils. This was firstly attributed to a greater initial content of organic matter in such soils, but also to a reduced absorptive capacity of minerals resulting in poorer NOM retention (Tipping et al., 1999). Recent research also indicates a trend towards increasing DOC concentrations in surface waters in the majority of the UK, with a 77% upward trend in DOC concentration since 1961. Trends are attributed to climatic changes (temperature increases and the frequency of severe droughts) as well as land use changes and most recently a rise in deposition-driven rainwater and soil acidity, influencing organic matter solubility and

potentially increasing DOC export to the sea (Chapman et al., 2008, Monteith et al., 2007, Worrall and Burt, 2007).

From the literature, it is evident that seasonal variation in NOM is as dependant on source as composition. Uncharacterised variations in NOM content would create more difficult treatment conditions at WTW as the source of coagulant demand and optimal DOC removal conditions would be largely unknown. Upward trends in DOC concentration of surface waters also pose a treatment risk as many WTW would have limited capacity to increase NOM removal without having informed implementation strategies in place. The composition of NOM is therefore an integral factor in understanding treatment capacity.

2.2 Characterisation of NOM

Identification of NOM characteristics is an essential tool in understanding the functionality and influences of NOM in an aquatic system, and subsequently provides insight into removal potential and DBP formation in water treatment and supply. Formation and composition of NOM in surface waters can alter substantially between catchments due to spatial and temporal variation, therefore there is no definitive representation of NOM. Characteristics including size, structure and charge density are useful distinguishing parameters which have been utilised in recent characterisation investigations as a basis to further understanding of NOM complexity (Frazier et al., 2003, Thomsen et al., 2002, Rodriguez-Zuniga et al., 2008).

2.2.1 Existing characterisation methods

A wide range of characterisation tools are available for the identification of NOM components. Characterisation tools can be split into four tiers of analysis; preliminary characterisation, size characterisation, chemical identification and behaviour and finally, spectral signature (table 2.1). Preliminary characterisation tools include TOC/DOC, suspended solids concentration and ultraviolet absorbance (UV). Preliminary analysis typically focuses on the dissolved fraction. Although there is no generally accepted cut-off between colloidal and particulate matter (Peuravuori and Pihlaja, 1997), most modern literature refers to dissolved as the size fraction below 0.45 µm, constituting >90% of NOM (American Water Works Association Research Foundation/Croue, 2000). The complex nature of NOM composition therefore requires more sophisticated analytical techniques which differentiate upon physio-chemical properties. Such techniques are predominantly laboratory based with extensive sample preparation. Typical NOM characterisation methods are considered in the following section.

2.2.2 Membranes

Many laboratory techniques for NOM characterisation require isolation of NOM prior to analysis. Isolation of NOM fractions is commonly performed using membrane technology or absorption onto resins. Membrane technologies such as ultrafiltration (UF) and reverse osmosis (RO) differentiate NOM fractions using molecular weight (MW) in a pressure-driven process (Kitis et al., 2002). UF is a physical separation process which has been widely used since the 1970s (Schwede-Thomas et al., 2005). UF's popularity resides with its ease of use and ability to handle large sample volumes (Assemi et al., 2004). Hydrophobicity, charge and steric effects of particles can influence results so NOM is rarely excluded on size alone

(Pelekani et al., 1999). Another problem associated with UF resides with inconsistent production of NOM fractions (Assemi et al., 2004), as although production of commercial membranes impose nominal MW cut-offs, calibration is performed using macromolecules such as proteins, and sugars and polysaccharides for smaller pore membranes (Pelekani et al., 1999, Kitis et al., 2002). NOM structural characteristics that are comparable to calibration materials often result in the rejection of DOM components, producing fractions not within the expected size ranges (Alberts et al., 2002, Assemi et al., 2004), and can create high aggregates of solutes blocking membrane pores (Peuravuori and Pihlaja, 1997).

2.2.3 Resins

Isolation and basic characterisation of NOM according to HPO and HPI properties are performed by Amberlite XAD resins. In a technique developed by Malcolm and McCarthy, fractions of HPO acids (XAD-8 absorbable), HPI acids (XAD-4 absorbable) and HPI neutrals (neither XAD-8 nor XAD-4 absorbable) are frequently reproduced in NOM characterisation studies (Malcolm and MacCarthy, 1992, Maurice et al., 2002, Her et al., 2008, Zhang et al., 2008). Resin fractionation is a widely used and accepted method of separating NOM fractions into bulk properties, however disadvantages of the process have been highlighted in a number of recent literature studies that cast a degree of scepticism over results. Croué et al., (2000) reported that 15-30% of NOM was not retained by fractionation protocols in a study that backed up findings by Le Cloirec et al., (1990) where poor HPI adsorption was observed. Most recently, Bond et al., (2009) observed that even with the most hydrophobic of compounds, tannic acid, had a 7% recovery in the HPI fractions, with a similar situation experienced with aspartic acid, a very hydrophilic compound. A recent review of NOM

characterisation methods also raised issues regarding the pH of the sample (in order for particles to adhere to the resins, the sample pH must be reduced to 2) resulting in possible chemical or physical alterations of NOM and irreversible adsorption of NOM compounds to resins (Matilainen et al., 2011).

2.2.4 High performance size exclusion chromatography (HPSEC)

High performance size exclusion chromatography (HPSEC) is a size exclusion mechanism operating at high pressure and requires minimal sample volume. HPSEC distinguishes between molecular size using a porous gel with a controlled pore size distribution to separate between molecules (Pelekani et al., 1999). Small molecules access more of the internal pore volume of the gel column and larger molecules are unable to penetrate into the gel pores so are eluded from the column first, followed by the smaller particles (Chow et al., 2005, Matilainen et al., 2002, Vuorio et al., 1998, Pelekani et al., 1999). A typical HPSEC chromatogram with peaks assigned is shown in figure 2.1. As with UF, factors such as molecular structure, steric effects and hydrophobicity may influence results (Matilainen et al., 2002) and comparability of results due to individual calibration techniques is limited. A 2003 study by Wu et al., (2003) concluded HPSEC characterisation is preferentially limited to smaller MW fractions as the HPO nature of larger MW fractions causes them to strongly absorb onto the HPSEC column. A number of different elutents are available, however interactions with NOM have been recorded for both polymer-based and silica-based columns (Specht and Frimmel, 2000).

HPSEC has however become very useful for NOM characterisation during drinking water treatment (Chow et al., 2008c, Fabris et al., 2008), with results also shown to correlate with DBPFP and other MW technologies (Assemi et al., 2004, Egeberg et al., 2002, Korshin et al., 2009). With the use of data analysis tools, it can provide a detailed picture of NOM components on raw water and through the water treatment process.

2.2.5 Nuclear magnetic resonance spectroscopy (NMR) and gas-chromatography mass-spectrometry (GC-MS)

Identification of the chemical make-up of NOM is performed using techniques such as Nuclear Magnetic Resonance (NMR) spectroscopy, Gas-Chromatography Mass-Spectroscopy (GC-MS) and Fourier Transform Infrared (FT-IR). In GC-MS, following a similar principle to HPSEC, molecules are eluted from the gas chromatograph according to their physical properties. Once eluted from the column, molecules are captured and ionised in the mass spectrometer and identified using their mass charge ratio (American Water Works Association Research Foundation/Croue, 2000). Although not strictly a quantitative analytical technique, GC-MS has been successful in identifying the distinctions between humic substances, the identification of aromatic structures (large peaks of phenol and cresol) and identification of the lignin, carbohydrate and protein derived compounds in NOM samples (Peschel and Wildt, 1988, Croue et al., 1993, Frazier et al., 2003). Application of GC-MS in the study of organic matrices has been successfully applied in a number of surface water studies (Frazier et al., 2003, Widrig et al., 1996) and a study by Vilge-Ritter et al. (1999) utilised the procedure to highlight preferential removal between iron and aluminium coagulants (Vilge-Ritter et al., 1999a).

Applied to water treatment processes, NMR characterisation technology has identified the removal of aliphatics over aromatics in HPO NOM molecules due to the interaction with aluminium hydroxides in chemical coagulation (Kim and Yu, 2005). The use of NMR by Thomsen et al. (2002) identified increased content of carboxyl carbons and carbohydrates in fulvic acids over humic acids. ^{13}C NMR also provides an aid for interpretation of results for emerging characterisation technologies such as field flow fractionation (FIFFF) (Assemi et al., 2004, Matilainen et al., 2011).

2.2.6 UV and specific ultraviolet absorbance (SUVA)

UV absorbance at a wavelength of 254 nm is widely attributed to the aromatic chromophores (light absorbing units) present in NOM at varying degrees of activation (Korshin et al., 2009), and has been widely used as a surrogate for DOC concentration and reactivity (Tipping et al., 2009, Chow et al., 2008a). UV_{254} is widely used in WTW as a representation of NOM aromaticity, and is used as a predictor of THM (American Water Works Association Research Foundation/Croue, 2000). Research by Matilainen et al., (2006) and Korshin et al., (2009) highlight potential disadvantages of UV_{254} when using it as a predictor of DOC and THM formation. Small aliphatic compounds have a lack of conjugated double bonds which are non UV-light absorbing and would not be accounted for in UV_{254} measurements (Matilainen et al., 2006). Differences in DOM properties mean that UV_{254} absorbance and $SUVA_{254}$ can only be an approximate method of DOC and THM (Tipping et al., 2009).

Development of SUVA as an operational indicator by Edzwald in 1985 relates NOM composition to ease of removal by typical coagulation and flocculation mechanisms (table 2.2). Specific ultraviolet absorbance (SUVA) is the ratio of UV to DOC and is well correlated to the aromatic content of NOM (Fabris et al., 2008). Several researchers have identified strong correlations with DBP formation potential and the ability for NOM removal by coagulation (Bose and Reckhow, 2007, Kitis et al., 2001, Kitis et al., 2004, Jung and Son, 2008). Contrasting research on potential links with SUVA however show a lack of correlation with the formation and precipitation of THM and HAA (Ates et al., 2007a). Several authors (Ates et al., 2007a, A. et al., 2004) reported that there was no observable relationship between $SUVA_{254}$ or UV_{254} and THMFP in waters with a lower SUVA value than 3 L mg^{-1} m^{-1}, suggesting that previously reported relationships may be water specific. Ates et al., 2007 proposed that $SUVA_{254}$ does not capture the reactive sites of NOM that are responsible for DBP formation. Weishaar er al., (2003) also states that SUVA appeared to be a better indicator of the reactivity of the humic components of NOM than the total DOC present. It is entirely plausible that the use of UV_{254} and $SUVA_{254}$ methods for DBPFP may significantly underestimate the number of DBP formed and therefore the associated risk.

2.2.7 Fluorescence spectroscopy

Fluorescence spectroscopy has attracted increased attention in the water industry in the last 20 years due to its ease of use, rapid analysis and better sensitivity and selectivity (Bieroza et al., 2009b, Bridgeman et al., 2011, Henderson et al., 2009, Matilainen et al., 2011, Peiris et al., 2010). 3D scans have also been developed in the last decade, providing a more comprehensive analysis than the previous single-scan method (Spencer et al., 2007).

A fluorescence signature occurs when an electron in an atom or molecule is excitated to a higher energy level by the absorption of energy when exposed to ultraviolet light (Hudson et al., 2007). NOM fluorescence is attributable to structural characteristics in aquatic humic and fulvic acids, inductive of source organic material (Baker et al., 2008, McKnight et al., 2001). Fluorescence spectroscopy is a rapid technique requiring minimal sample preparation (Henderson et al., 2009) and correlation of fluorescence peaks with TOC (>0.8 R^2 correlations reported by Hudson et al., 2008), organic precursors and the total TOC removal (0.9 R^2 reported by Beiroza et al., 2009b) have increased the use of fluorescence spectroscopy in NOM characterisation studies.

Excitation emission matrices are created through intensity scans, with fluorescent peak location associated with humic-like, tyrosine-like, tryptophan-like or phenol-like compounds (Chen et al., 2003), with typical peaks found in natural waters are listed in table 2.3. Peak T intensity is an indicator of the HPI amino acid-like fraction and anthropogenic NOM inputs (Bieroza et al., 2009b), and occurs at an excitation wavelength of 280 nm and emission wavelength of 350 nm. Peak C intensity is an indication of fulvic-like fluorescence material, with peaks occurring within a range of 300-340 nm excitation, 400-460 emission. An example of a typical raw water EEM with peaks identified is shown in figure 2.2.

Fluorescence spectroscopy is a rapid analysis tool compared to laboratory based tools such as HPSEC and resins, and can be directly employed on site (table 2.1). Progress could however be hindered due to lack of understanding of the technology and interpretation of results.

2.3 Potential NOM characterisation methods

The characterisation methods previously discussed have an intrinsic value to the identification of NOM, however none has the ability to provide a full picture of NOM in surface waters or provide a concrete link between NOM and DBP. A robust method of characterisation can provide an insight into potential NOM removal and the associated DBP formation rate, which is increasingly becoming a required commodity by WTW due to the recent changes in Regulation 26, requiring all DBP to be monitored and reduced. Potential new NOM characterisation techniques such as carbon isotope analysis and environmental colloid characterisation are presented here as two new characterisation techniques and are used to characterise NOM in surface waters and through the water treatment process.

2.3.1 Carbon isotopes

Carbon isotopic analysis of the radioactive and stable isotopes of carbon (^{14}C and ^{13}C respectively) can provide valuable information on catchment source, carbon age and estimating turnover times of organic matter in aquatic systems (Austnes et al., 2010, Raymond and Bauer, 2001b). Organic matter ^{14}C reflects the activity of atmospheric CO_2 at the time it was fixed. Atmospheric testing of nuclear weapons carried out during the 1950s to 1960s released large amounts of ^{14}C to the upper atmosphere, referred to as 'dead' carbon (Tipping et al., 2007). This ^{14}C was rapidly oxidised to $^{14}CO_2$ and incorporated into the global carbon cycle and resulted in low-level global ^{14}C contamination. Atmospheric ^{14}C values peaked in 1964 and have been falling since then (Figure 2.3). Due to this, ^{14}C values above 100% modern carbon are classed as being produced after 1950. ^{13}C values are used

to determine the source or sources of organic carbon (e.g. terrestrial derived organic matter ^{13}C values typically range from -24 to -32 ‰$_{(VPDB)}$). Deviation from an expected value could be due to addition of carbon from another source or isotopic fractionation during chemical or biological processing. Investigations into NOM source and age could provide an insight into the formation conditions of NOM, and how it is reacts to water treatment processes. Investigations between NOM age and DBPFP also need to be considered.

Carbon isotopic analysis of DOC in surface waters began in the early 1980s with studies by (Hedges et al., 1986), reporting on temporal changes in carbon isotope signatures. These studies also identified that terrestrial DOC exported to rivers is younger (^{14}C enriched) than the soil from which it originated. Terrestrial soils are estimated to store between 1300 to 1500 x10^{15} g of carbon (Schkesinger, 1977, Post et al., 1982), 200 times the amount of CO_2 released into the atmosphere through the burning of fossil fuels (Trumbore et al., 1989). DOC is leached from soils into rivers and estuaries through chemical and mechanical weathering processes, and an estimated 0.4 x10^{15} g of organic carbon is transported in particulate and dissolved forms to the world's oceans annually (Spitzy and Ittekkot, 1991, Raymond and Bauer, 2001a).

Recent literature now suggests that Northern European and America surface waters have seen substantial increases in DOC concentrations (Sickman et al., 2010, Evans et al., 2007). In the UK, Freeman et al., (2001) and Worrall et al.,(2004) recorded an average increase of 100% in upland DOC concentrations, and as most of the UK soil carbon is contained in upland soils (Austnes et al., 2010, Tipping et al., 2007), rises in DOC levels are already having a detrimental effect on the efficiency of current water treatment processes. The causes of

the increases in DOC in riverine systems are still unclear, however Bellamy et al., (2005) attributes a loss of carbon in the soils of England over the past 25 years to climatic warming. This is contradicted by Evans et al., (2007), stating that although increases in global temperatures could affect the de-stabilisation of soil DOC stocks, they are unlikely to cause such a large increase in riverine DOC. The study proposed instead that the majority of the increase could be attributed to increased agricultural activity since the 1970s causing destabilisation of soil carbon and a loss of older carbon in soils (Evans et al., 2007).

Of the small number of studies conducted into carbon analysis of surface waters in the UK, only three identify variations in $\delta^{13}C$ (Tipping et al., 2009, Billett et al., 2007, Waldron et al., 2009). Tipping *et al.* (2009) observed isotopically lighter ^{13}C material dominant in high discharge events, with heavier ^{13}C at low flows. This is in accordance with an earlier investigation on carbon in surface waters, where it was observed that ^{13}C was more enriched in late spring and summer (Ziegler and Brisco, 2004).

Literature on carbon isotopic analysis of DOC in UK surface waters remains in the minority and is dominated by only a handful of authors, and carbon isotopes in the water treatment process is an area which has not yet been investigated but could provide a valuable insight into NOM source and turnover. Investigations between NOM age and DBPFP also need to be considered.

2.3.2 Environmental colloids analysis

Natural environmental colloids are materials within the 1 nm to 1 µm size region (figure 2.4) and have differing transportation and behavioural qualities to particles (which have a dimension greater than 1 µm) (Lead and Wilkinson, 2006). Environmental colloids are highly reactive and influence the fate and behaviour of trace pollutants in natural waters (Newman et al., 1994, Baalousha and Lead, 2007). It is thought that the number of small environmental colloids in surface waters is far greater than the number of particles (e.g. 10^6 times more 10 nm colloids than 1 µm particles) (Lead and Wilkinson, 2006). The study of environmental colloids is greatly hindered by their instability and profound complexity, coupled with a lack of efficient methods to fractionate and characterise environmental colloids (Baalousha and Lead, 2007, Lead and Wilkinson, 2006). Even less well understood is the effect of NOM coating of inorganic colloids and how this affects the stability, mobility and interactions with trace elements (Lead and Wilkinson, 2006).

Over the past fifteen years, improvements in analytical techniques mean the development of environmental colloids analysis has increased intrinsically. Early studies by Wilkinson (1997) on colloidal NOM found pedogenic and aquagenic NOM not only had differing physiochemical structures, but differing behavioural properties in terms of sedimentation rates. Wilkinson also acknowledged that a higher proportion of humic substances increased particle stability and promoted bridging bonds and aggregation of colloidal material. An earlier investigation by Buffle and Leppard in 1995 observed how fulvic acids aggregated onto the surfaces of larger colloids to influence aggregation mechanisms.

Developments in imaging techniques such as nanoparticle tracking analysis (NTA) and atomic force microscopy (AFM) have revolutionised investigation into environmental

colloids shape. Once thought of as circular and impermeable, colloidal organic carbon aggregates into chain-like structures and also fibular and spongy structures which are highly porous (Buffle and Leppard, 1995, Wilkinson et al., 1997b). AFM imaging has also recently indicated that colloids smaller than 50 nm represent the bulk of the colloidal fraction which is in turn now known to represent a large proportion of the dissolved fraction of NOM (Lead and Wilkinson, 2006). There are a number of limitations for environmental colloid characterisation technologies however; sample preparation procedures are one of the major obstacles for AFM techniques as samples need to adhere onto mica sheets prior to drying (figure 2.5). It is unlikely that all colloids are adsorbed onto the mica sheet, and drying processes could alter colloidal shape, giving an unrepresentative sample. A major limitation for DLS is that average particle size measurements are preferential towards larger particles so give misleading average particle size measurements.

After decades of research, the role of environmental colloids in aquatic systems is still thought of as poorly defined (Lead and Wilkinson, 2006). The behaviour of environmental colloids through surface coating and aggregation and sedimentation mechanisms could greatly affect coagulation removal efficiency.

2.4 The impact of NOM on the water treatment process

In modern water treatment practices the presence of NOM can negatively affect treated water quality and if incompletely removed, through the water distribution system. The presence of NOM, aside from the obvious taste and aesthetic issues, can impact water treatment. Incomplete removal of NOM in the coagulation stage can cause increased

membrane fouling and increased filter backwashing and block activated carbon pores, hindering the removal of taste and odour forming compounds (Fabris et al., 2008). In the final disinfection stage, NOM not removed by previous treatment processes reacts with chlorine to form potentially carcinogenic disinfectant by-products (DBP) such as trihalomethanes (THM) and haloacetic acids (HAA). A continued reaction between free residual chlorine and NOM through the distribution system and a routine dosing of chlorine and strategic points within the distribution system can lead to higher DBP concentrations at consumer tap (Baytak et al., 2008). NOM also supports microbial growth in the distribution system by acting as a food source (Frazier et al., 2003).

2.4.1 Formation of disinfectant by-products

Widespread use of disinfection in the early 20th century dramatically reduced the outbreaks of waterborne illnesses such as typhoid and cholera, and due to its effectiveness, has remained the most popular method of cleansing to this day (Moudgal et al., 2000). The identification of the first DBP in chlorinated drinking water in the USA and Holland in 1974 sparked a global interest on what was to become a major public health issue (Rook, 1974, Bellar et al., 1974, Richardson, 2003). Widespread identification of DBP such as the THM chloroform by the United States Environmental Protection Agency (USEPA) in 1976 coupled with studies linking chloroform to cancer in lab animals (NCI., 1976) and cancer mortality rates have prompted interest in this area (Calderon, 2000).

To date, 600-700 DBP have been reported in the literature (Nieuwenhuijsen et al., 2009, Malliarou et al., 2005, Chen et al., 2008, Krasner et al., 2006, Ates et al., 2007b). THM and

HAA are the most commonly detected and of the highest concentration in chlorinated waters (Chen et al., 2008). DBP formation is not confined to chlorinated disinfectants however, DBP are reported for all the major disinfectants such as ozone, chlorine dioxide and chloramines (table 2.5) (Krasner et al., 2006). Due to their strong oxidising nature, disinfectants react with NOM, bromide, iodine and background pollutants that may be present, leading to the formation of complex and highly variable DBP. Subsequently, although a large number of DBP are recorded in the literature, DBP are still poorly characterised with limited precursor identification (Weinberg, 2009).

The work recorded in this thesis deals primarily with the identification of THM and HAA precursors, and as such the literature review shall focus on these compounds in the following sections.

2.4.2 Trihalomethanes and haloacetic acids

THM and HAA are the two most prevalent DBP formed by chlorine disinfection on a weight basis (Krasner et al., 2006). Electrophilic aromatic substitution, electrophilic addition and oxidation are among the reactions that occur between disinfectants and precursors such as NOM to form DBP (Weinberg, 2009). Studies into THM and HAA show formation is known to be affected by pH, temperature, nature and concentration of NOM, disinfectant type and dose, reaction time and bromide concentration (table 2.5) (Roccaro et al., 2008, Serrano and Gallego, 2007, Nieuwenhuijsen et al., 2009). NOM concentration however, in combination with Cl_2 dose, is believed to be the most significant parameter (Kitis et al., 2002, Chang et al., 2001b). Chlorine disinfectants are known to react with both phenolic and non-phenolic

(including both aromatic and non-aromatic) of NOM but formation varies with NOM composition (Weinberg, 2009).

Investigations into THM precursor affinity and aromaticity studies conducted by Croue *et al.,* (1993) and Kitis et al., (2002) demonstrated that the HPO fraction of DOM were the most reactive components and produced the most active precursor sites, therefore having the greatest potential to form halogenated DBP. Research published by Goslan et al., (2009) investigated further, finding that THM formation was higher in humic-rich waters compared with fulvic-rich waters. A contrasting review of DBP formation by Bond et al., (2009), found that there was no significant relationship observed with the physical properties of NOM and the formation of DBP. It was in fact suggested that one DBP may be the precursor for another type of DBP (Bond et al., 2009). Seasonally, THM levels are reported to be higher in the summer months (Krasner et al., 2006, Uyak and Toroz, 2007, Rodriguez-Zuniga et al., 2008, Williams et al., 1998). This is attributed to an increased organic matter content in surface waters (Baytak et al., 2008).

Research interest into THM formation remains high as less than half of the halogenated by-products from chlorination have been identified (Weinberg, 2009) but even less is known about HAA formation. This is presumably largely attributable to a current lack of regulatory limits and very little data had been published on HAA levels in the UK in scientific literature before 2005. Research by Goslan et al., (2002, 2009), Malliarou et al., (2005), Bougeard et al., 2008, Bond et al., 2009 and a recent report on the formation and occurrence of haloacetic acids in UK waters for the DWI (DWI et al., 2009) have provided a wealth of new information regarding HAA formation and levels in UK waters. HAA are carboxylic acids and

are often reported to be as prevalent as THM (Bougeard et al., 2010) and aspartic acid is the main precursor for HAA formation (Bond et al., 2009). There appear to be few similarities between the two sets of DBP however, and concentrations of HAA decrease with increased residence time in distribution systems (Malliarou et al., 2005, Kim and Yu, 2005, Lee et al., 2003). Seasonal variations in HAA formation found increased rates of formation in the summer and autumn months compared with levels recorded in winter and spring (DWI et al., 2009). The DWI report (2009) into HAA formation in UK drinking water found an increase of 65 and 85% in HAA formation in autumn months compared to spring and winter. It is known that HAA formation is largely dependent on temperature and pH, with increases of 14% in HAA formation being recorded in upland waters with an increase from pH 6 to 8 (Bougeard et al., 2008). The DWI (2009) report into HAA formation in drinking water found increased HAA formation in lowland reservoir sources and groundwaters. Also, research published by Bougeard et al., (2008) found the formation of HAA in lowland waters were more susceptible to changes in pH due to the type of organic material responsible for HAA formation. Water treatment also impacts on the formation of HAA, as an increase in HAAFP was reported due to partial biological and chemical oxidation of NOM molecules, and the HAAFP of HPI compounds were found to increase after treatment (Bond et al., 2009, Reckhow and Kim, 2008).

The formation of DBP is so intrinsically dependant on the formation conditions, NOM components and treatment and distribution conditions that prediction of DBP is exceptionally difficult at WTW, so any method of DBP prediction and removal strategies would be a valuable tool for any WTW.

2.4.3 Regulations and limits

The first regulations to limit THM were introduced by the US EPA in 1979 after epidemiology studies on laboratory animals found links between chloroform and cancer (Serrano and Gallego, 2007). An initial total THM (TTHM) regulation limit of 100 μgL^{-1} was introduced by the US EPA on quarterly samples at consumer tap but this did not include HAA. This has since been revised, with current regulatory limits at 80 μgL^{-1} for TTHM and 60 μgL^{-1} for HAA_5.

In 1989 a 100 μgL^{-1} regulation limit for THM was introduced. Again, there was no inclusion of HAA regulation at this initial stage. Further revisions of water regulations by the DWI in 2000 failed to reduce TTHM limits or introduce HAA monitoring, following precedence set by the European Union Drinking Water Directive. Sampling frequency is dependent on population size (DWI, 2010), so areas of low population numbers could suffer from inadequate sampling, letting potentially high THM levels go unrecorded. A vital difference between UK and US regulations is that UK regulations are absolute standards at the time of sampling i.e. all exceedances over 100$\mu g\ L^{-1}$ are to be reported, whereas US regulations record a rolling average over a year time period. An absolute figure recording system leaves UK water companies with a higher risk of breaching DBP limits compared to US WTW. Although there was no inclusion of HAA monitoring in the most recent revisions, a recent DWI report listed the five HAA compounds as 'a high priority' to be routinely monitored (DEFRA/DWI, 2008, DWI et al., 2009).

The World Health Organisation (WHO) is the foremost guide on THM and HAA regulator guidelines however, regularly producing MCL guidelines for DBP. Details of current WHO guidelines and US and UK regulations and can be seen in table 2.6.

2.4.4 Epidemiological studies into THM and HAA

Despite numerous studies into the epidemiology of DBP, concrete links between DBP and adverse health effects are few and invariably open to personal interpretation. To date, the mechanisms by which DBP have the potential to cause adverse health effects and the range and extent of these health effects have been well investigated. Links have been made between DBP and cancers in the bladder, colon-rectum, stomach and rectal and leukaemia (Calderon, 2000). Literature also reports links with adverse reproductive outcomes such as spontaneous abortion, birth defects and low birth weights (Nieuwenhuijsen et al., 2009, Hrudey, 2009, Baytak et al., 2008). Major reviews by Nieuwenhuijsen et al. (2009) and Richardson et al. (2007) acknowledged that links between DBP and adverse health effects do occur, but highlighted many of the inconsistencies and limitations of the studies, the first of which being a limited study of chemicals.

Chlorinated DBP, especially chloroform, remain the focus of the large proportion of epidemiology studies, with very few focusing on the possible adverse effects of HAA. Researchers are now of the view that N-Nitrosodimethylamine (NDMA), and Haloacetronitriles (HAN) pose a greater health risk as they are more potent at lower quantities due to their mutanogenic and carcinogenic effects (Robinson et al., 1986, Hrudey, 2009, Sirivedhin and Gray, 2005).

The most limiting factor in epidemiology studies is an inability to determine exposure routes and provide suitable sample sizes over an adequate time period. From the literature, three messages become clear; the first is that there are substantial causes for concern about the exposure to DBP formed in the final stage of the drinking water treatment process; the effects of which can be seen more prominently in the young and old and with pregnant women and their developing foeti (Calderon, 2000, Roccaro et al., 2008, Hua and Reckhow, 2007, Nieuwenhuijsen et al., 2009). Secondly, inhalation is the major exposure route for chlorinated DBP with the risks of far outweighing those from oral consumption (Wang et al., 2007). Finally, there is a significant knowledge gap with regards to the identification of DBP and subsequent epidemiological studies. Until a definitive way of estimating exposure is found, we are unlikely to have conclusive knowledge as to the real threat of DBP exposure.

2.5 Current NOM removal

Conventional surface WTW employ a variety of processes which are split into upland or lowland treatment models. Chemical coagulation was initially intended to facilitate the removal of turbidity and the removal of NOM by activated carbon adsorption (Hall and Hyde, 1992). The identification of NOM as a THM precursor gave rise to coagulation by metal salts followed by a solid-liquid separation process such as sedimentation or dissolved air flotation (DAF) to become the standard process for bulk NOM removal (Fabris et al., 2008, Sharp et al., 2006c). Thanks to early investigations by Croue et al., (1993) and an extensive review of coagulation in terms of particles, organics and coagulants by Edzwald (1993), coagulation is now a well understood and practised process (Jarvis et al., 2008). An

increased loading of DOC in autumnal flushes events and more intense examinations of DBP regulations has led to the review of current water treatment practices and the development of viable alternatives.

2.5.1 Coagulation

Coagulation and flocculation is considered to be an important process in the drinking water treatment industry because of the obtainable percentage of removed matter (Ratnaweera et al., 1999). The principle of coagulation and flocculation is to facilitate the removal of turbidity, colour and organic and inorganic pollutants by aggregating finer particles and colloids into larger particles called flocs through destabilisation and precipitation mechanisms (Duan and Gregory, 2003, Jarvis et al., 2005c). Coagulants such as ferric sulphate ($FeSO_4$) and aluminium sulphate (or "alum", $Al_2(SO_4)_3 \cdot 14H_2O$) are added at the coagulation stage in order to improve floc structures, making them stronger and larger. The majority of particles in water exhibit a negative surface charge which dominates any attractive forces between particles, impeding the formation of large flocs. The addition of coagulant aims to reduce electrostatic repulsion, improving the formation of flocs (Duan, 2003). The addition of organic polymers with either positive or negative charges to improve NOM floc structural character is commonly practised in WTW (Gray, 2005, Jarvis et al., 2005c). The formation and later removal of NOM flocs through coagulation/flocculation can be performed through several mechanisms:

1) Charge neutralisation; cationic metal interacts electrostatically with NOM, adsorbing onto the partides and neutralising particle charge and promoting floc formation (Chow et

al., 2004, Sharp et al., 2006c). Charge neutralisation is commonly performed at a lower pH, promoting the use of less coagulant and sludge production.

2) Adsorption of NOM onto metal hydroxide precipitates (Chow et al., 2004).

3) Sweep flocculation; NOM is removed from suspension from entrapment by the formation of an amorphous hydroxide precipitate (Duan and Gregory, 2003).

Ferric sulphate and alum are the most commonly used coagulants in the UK water industry (Matilainen et al., 2010, Duan and Gregory, 2003). Flocs formed from iron salts have been shown to be larger and more numerous than alum flocs, resulting in improved performance (O'Melia et al., 1999, Sharp et al., 2006b). This is in agreement with the findings by Matilainen et al., in 2005 which found on average a 10% increase in DOC removal by ferric sulphate over alum. Kabsch-Korbutowicz (2005) defends the use of alum over ferric, stating that alum coagulantion is dominant in higher pH waters and in sweep flocculation. DOC removal using alum is not effective at pHs lower than six, so for low pH coagulation iron based coagulants are used (Fusheng et al., 2008, Gregor et al., 1997, Uyak and Toroz, 2007). Table 2.7 illustrates the strengths and weaknesses of individual coagulants and polymers that are available to be employed in UK coagulation processes.

Floc size and strength are crucial factors in flocculation that are influenced by NOM. Floc strength is defined by Jarvis et al., (2005) as 'the energy required to break flocs under tension, compression or shear'. Floc size and strength are interrelated as larger flocs generally tend to be weaker and break easier in high shear conditions (Sharp et al., 2006a, Jarvis et al., 2005a, Jarvis et al., 2005c, Wilkinson et al., 1997b). Jarvis et al., (2006) recorded floc sizes of 650 µm with NOM rich flocs, which decreased to approximately 450µm when

exposed to shears stresses formed in a jar test vessel with paddle rotations of 100-200 per minute (rpm). Smaller flocs are more stable as they are not affected by microscale eddies in the water (Jarvis et al., 2005c), tending to be caught up within them rather than being broken down by them. NOM affects floc size and strength by coating the particles, reducing attraction forces. 'Flocs formed from waters of high colour and high NOM content are widely recognised as being fragile structures when compared to other flocs' (Jarvis et al., 2005b). This produces smaller flocs that break easily due to a lack of bridging bonds between molecules (Sharp et al., 2006a). Literature also suggests that floc formation is temperature dependent, with smaller flocs formed at lower temperatures which then negatively impacts on turbidity removal (Fitzpatrick et al., 2004, Matilainen et al., 2005).

The extent of NOM removal is greatly affected by the nature and dosage of coagulant (Uyak et al., 2007, Szlachta and Adamski, 2009). Literature has repeatedly demonstrated that the larger MW components of NOM are more readily removed in coagulation/flocculation processes (Chang et al., 2001a, Edzwald, 1993, Kabsch-Korbutowicz, 2005, Matilainen et al., 2002, Matilainen et al., 2005, Sharp et al., 2006c). The low MW, HPI fraction of NOM has little charge density and is therefore least amenable to removal by coagulation and as such, the HPI content of NOM acts as a good indicator for the residual DOC concentration after treatment (Fabris et al., 2008, Sharp et al., 2006a). NOM has however been credited with controlling particle stability in cases of high NOM concentrations due to steric interactions between NOM-coated surfaces (Walker and Bob, 2001). With larger particles, there are stronger Van Der Waals attractive forces. The addition of a NOM layer acts as a repulsive force, counteracting the Van Der Waals attractive forces and thereby stabilising the particles

(Walker and Bob, 2001). This interaction however is hugely dependant on the concentrations of different types of NOM.

In order to improve removal of the low MW HPI NOM existing coagulation methods need to be enhanced or optimised. The following sections examine approaches employed to increase NOM removal without installing new technology to WTW.

2.5.2 Enhanced coagulation

Chow et al. (2004) summarised the objective of enhanced coagulation as 'the modification of the coagulation process to achieve greater maximum NOM removal where greater doses of coagulant are used' (Chow et al., 2004). Enhanced coagulation is advocated by Uyak et al., (2007) and Hurst et al., (2004) as removal of DOC was increased from 45% to 76% in pilot plant testing and has long been a regulatory requirement in the US to remove DBP precursors (Edzwald, 1993). The overdosing of coagulant has a negative impact on floc structure however as excess precipitate interferes with electrostatic bonding (Bache et al., 1997). Enhanced coagulation is also more expensive as a greater amount of chemicals are needed, for both pH adjustment and coagulant and large amounts of solid waste are produced (Cromphout et al., 2008). Over-dosing of coagulant is proven to increase NOM removal compared to under-dosing but it is not a viable alternative due to cost and waste implications and it has a detrimental effect on charge neutralization, thus limiting effective removal of NOM.

2.5.3 Optimised coagulation

Optimised coagulation depends primarily on coagulation pH to achieve optimal NOM removal and as such, coagulant demand may be reduced.

The pH environment for NOM removal is one of the most important factors for optimum conditions (Gregor et al., 1997). It is widely recognised that optimal pH resides between 5-7 (Kabsch-Korbutowicz, 2005, Gregor et al., 1997, Vilge-Ritter et al., 1999b) and can be narrowed down further depending on the coagulant type. For example, alum coagulant optimum pH resides between pH 6 – 6.5 (Gregor et al., 1997, Qin et al., 2006), whereas ferric sulphate optimum pH has been recorded at 4.5, 5.2 and 5 (Jarvis et al., 2008, Qin et al., 2006, Gregor et al., 1997), although this does depend on source water type. Under optimal conditions, Qin et al., (2006) achieved 45% removal of DOC, and 97% turbidity in an organic rich surface water in Singapore. Above pH 6 however, removal efficiencies declined by up to 20%. Jarvis et al., (2008) achieved much higher removals of DOC (87-89%) for ferric based coagulant systems. pH affects both the surface charge and character of particles and as such increased NOM removal of the smaller MW HPI NOM components is achieved, whilst potentially lowering coagulant demand (Fusheng et al., 2008). Figure 2.6 illustrates that even at a low coagulant dose of 2 mgL^{-1}, low pH has a greater impact on NOM removal in all size fractions.

2.5.4 Charge control

The surface charge of particles in coagulation is a good indicator of the optimal conditions for coagulation. Zeta potential is a measure of a particle's outer surface charge and is

commonly related to the stability of the colloidal material under any given set of water characteristics (Sharp et al., 2006b). Sharp et al., (2006a) successfully demonstrated that a zeta potential within the range of -10 mv to +3 mv produce optimal removal efficiencies. Zeta potentials outside of this commonly have reduced NOM removal efficiencies (figure 2.7). Optimal conditions occur around zero mv, which can be achieved with alterations in pH and/or coagulant dosage (Ratnaweera et al., 1999).

Zeta potential clearly demonstrates a vital insight into the efficiency of NOM removal through coagulation and can highlight the effectiveness of any particular system during a specific time period, however online zeta potential measurements are often difficult to put into practice and would require constant monitoring of system performance. Zeta potential also cannot be relied upon as being the only indicator of coagulation performance as it only shows the status of the colloidal stability of the system, but not the amount of coagulant needed for colloidal destabilisation (Ratnaweera et al., 1999).

2.5.5 Two-staged coagulation

A final use of existing treatment practices would be two-staged coagulation where two coagulation/flocculation processes are employed and individually optimised. The first coagulation processes is targeted for removal of humic substances, usually at a lower pH of 4.8-5.1. The second coagulation process is for particulate removal at a much higher pH of 8.0-8.5 (Carlson and Gregory, 2000). A review of literature on two-stage coagulation by Fearing et al., (2004) observed removal increases from 50% to 90% and was most effective in humic-rich waters. Concerns were raised as poor removal of the fulvic acid fraction and

HPI neutrals resulted in no significant decrease in THM formation potentials (Fearing et al., 2004b). Staged coagulation did increase water treatability in most cases however, resulting in improved filter performance and longer filter runtimes (Carlson and Gregory, 2000), but it provided little additional improvement in the removal of low MW HPI NOM compared to existing coagulation and flocculation methods.

2.5.6 Granular activated carbon (GAC)

Activated carbon is the primary absorbent used for water treatment, and is typically employed for the removal of taste and odour compounds and pesticides (Bond et al., 2011). GAC media is composed of either wood, coal, coconut shells or peat and the media is 'activated' in a combustion processes to produce a highly porous media with a large surface area which adsorbs NOM (Hall and Hyde, 1992). NOM precursor removal by GAC absorption has previously reported a bulk DOC removal of 80%, THM precursor removal of 95% and HAA precursor removal of 89% (Jacangelo et al., 1995). These results were obtained by using a longer than average loading time (21 minutes), and treatment capacity was reduced to 42% DOC removal, 40% THM precursor removal and 71% HAA precursor removal after 250 days (Jacangelo et al., 1995). GAC is also effective at removing DBP already formed through pre-ozonation or pre-chlorination stages (Sani et al., 2008, Babi et al., 2007). GAC is normally used in filter beds or purpose-built adsorbers after sand filtration systems is more commonly found at lowland surface water sites as it is not deemed necessary at upland WTW where colour, turbidity and organics removal can more readily meet DWI regulations (Hall and Hyde, 1992).

Historically, literature relating to the removal of specific NOM fractions using GAC points towards the preferential removal of intermediate or small humic molecules (Matilainen et al., 2002, Vuorio et al., 1998) as smaller GAC pores were less accessible to high-MW compounds (Bond et al., 2011). In contrast, studies by Sani (2008), Gur-Reznik et al., (2008) and Cromphout et al., (2008), reported low efficiency of HPI NOM removal with GAC. Gur-Reznik *et al.,* (2008) described how HPI removal efficiency decreased considerably after a small number of bed volumes. This is in agreement with observations on a GAC pilot scale investigation by Vuorio et al., (1998) where the adsorption of larger particles was greater in newly regenerated columns, whilst towards exhaustion of the GAC column the smaller molecules were escaping from the column. In addition, the amount of smaller molecular fractions were occasionally increased, suggesting the presence of GAC fines in post-GAC samples (Vuorio et al., 1998). GAC media does have a limited lifetime, but depending on water quality and DOC loadings, the GAC breakthrough capacity can be up to one year (Hall and Hyde, 1992). The presence of GAC fines may be an area in need of further investigation, but in terms of DOC removal of the six WTWs selected for further investigation in Chapter 9, GAC removed an additional average of 18-42% of total DOC and would be considered a vital process at many of Severn Trent's surface water sites.

2.6 Linking the knowledge gap to the objectives of the thesis

The preceding sections have highlighted a number of areas of uncertainty in NOM characterisation and removal research. These are, in relation to the thesis objectives set out in Chapter 1:

(i) To evaluate the use of existing characterisation methods for the investigation of NOM composition and in the identification of key trends in NOM character, existing and achievable removal and DBP formation.

There is a wealth of research into NOM characterisation; however few studies have investigated NOM character and composition over a large number of surface water sites and a 24 month period. In scientific literature, the use of characterisation techniques such as UV, SUVA, fluorescence and XAD resins have been investigated heavily, but comparisons are rarely made between them in order to assess the suitability and/or limitations of each methods over a wide range of surface waters.

There is also increasing concern over the formation of disinfection by-products due the anticipation of more stringent regulations and the findings from epidemiological studies. Recent literature has identified a number of links between NOM composition and DBP formation, however DBP formation is still poorly understood and links are often site-specific. WTW are in need of robust methods for DBP prediction based on NOM character and treatment.

Hypothesis H1:

That existing NOM characterisation methods can discriminate between NOM character and removal at sixteen surface water treatment sites in the UK and provide a link with DBP formation.

Hypothesis H2:

Statistical analysis tools such as discriminant and PCA are more appropriate tools for the analysis of large data sets and can identify trends in NOM characterisation and links to DBP formation.

(ii) To investigate the potential for carbon isotopic analysis and environmental colloidal analysis as NOM characterisation tools, to address current characterisation needs and to identify trends with DBP formation.

A review of literature on NOM characterisation tools has identified that the HPI component of NOM is a major contributor to DBP formation but it is poorly quantified by the most commonly used NOM characterisation tools. Methods such as UV and SUVA omit non light-absorbing molecules, therefore presenting an incomplete view of potential DBP forming molecules, and TOC and DOC measurements do not give an insight into NOM components. Fluorescence spectroscopy has identified links with TOC removal, but the process is still being developed and is relatively unknown poorly understood in various parts of the water treatment sector.

The use of carbon isotopes and environmental colloidal analysis through WTW is a completely novel area of study. Carbon isotope techniques have been used to characterise catchment soil profiles since the 1980s, and have helped bring the major scientific issue of decreasing carbon in soil stocks to light. They have also been used in the investigation of DOC stocks in water, from rivers to estuaries, and there is a wealth of information on ocean carbon stocks. Carbon isotopes have not been used in the characterisation of NOM is surface waters in regard to water treatment however, and could provide a valuable insight

and a different angle into the character of surface waters in UK WTW. Environmental colloidal characterisation methods are still in a relatively new stage and although there have been some investigations into NOM character in surface waters, recent research defines this as an area that is still poorly defined. Carbon isotopic analysis and environmental colloidal analysis could increase the knowledge base of NOM composition and potentially link NOM composition to DBP formation.

Hypothesis H3:

Carbon isotopic and environmental colloidal analysis can be used for the identification of spatial and temporal variability in NOM and provide links with DBP formation.

Hypothesis H4:

Carbon isotopic and environmental colloidal analysis can identify the mechanisms of water treatment and discern the impacts on NOM components.

(iii) To establish whether current treatment conditions are capable of removing increased amounts of NOM in order to reduce DBP formation.

Process optimisation for the removal of DBP precursors is an area of great scientific interest and there are numerous studies into the possible ways of optimising removal using existing equipment and new technologies. Through critical analysis of the new technologies, few viable alternatives to the existing coagulation/flocculation techniques that are not without fault or induce great expense have been identified. One of the redeeming features for coagulation/flocculation processes is that it is an extremely well-understood and practised method. Unfortunately however, on most WTW it is not being used to its full potential.

There are many studies into the optimization of coagulation/flocculation, but most have been conducted in countries with characteristically different source waters. In the UK, there are a small number of authors who have conducted studies into low pH coagulation, but all the available studies have produced favourable results for DOC removal, and in turn, DBP reduction. Knowledge gaps lie within seasonal influences, and the costs and technicalities of initiating low pH coagulation on site. There is a need to provide a robust model incorporating DBP formation, NOM removal and cost that can display the achievable results for both high and low-DOC events.

Hypothesis H5:

Low pH coagulation can be used to increase NOM removal and minimise DBP formation so additional treatment options do not need to be explored.

Chapter 2 Figures

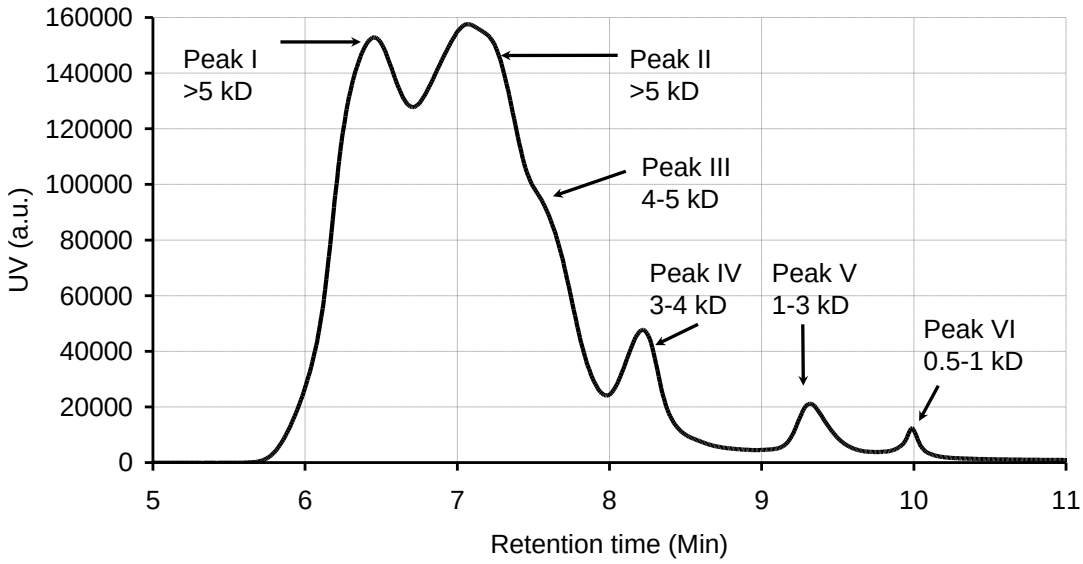


Figure 2.1 - Typical HPSEC chromatogram of raw water with peaks assigned (Pikkarainen et al., 2004)

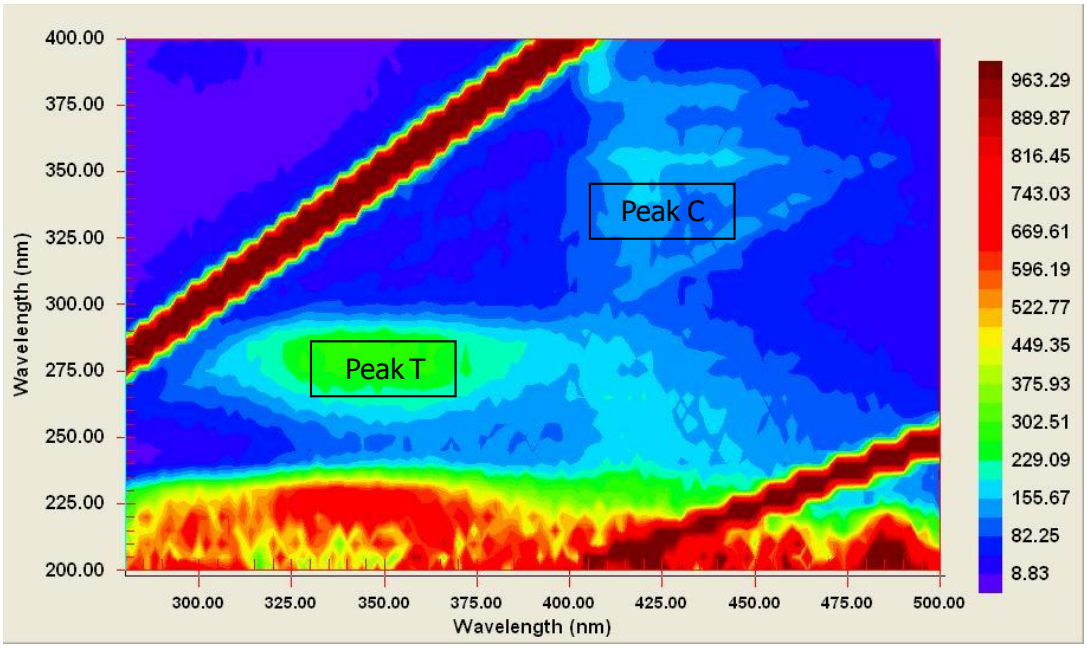


Figure 2.2 - Peak C and Peak T locations on a fluorescence EEM

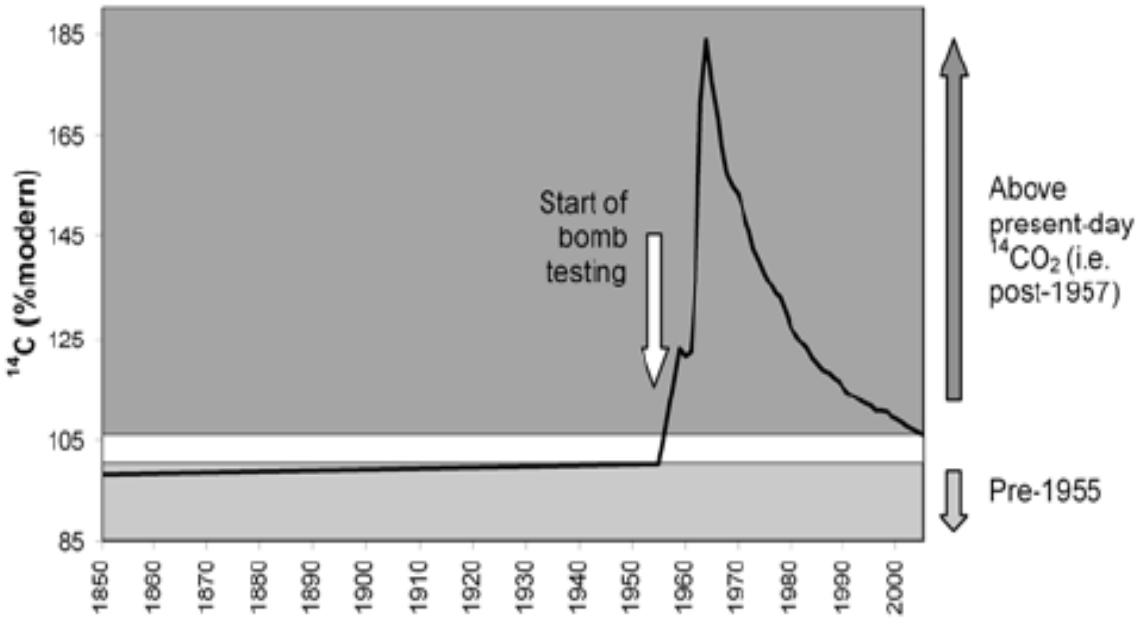


Figure 2.3 - The effect of bomb testing on ^{14}C percentage modern carbon signatures (Evans et al., 2007)

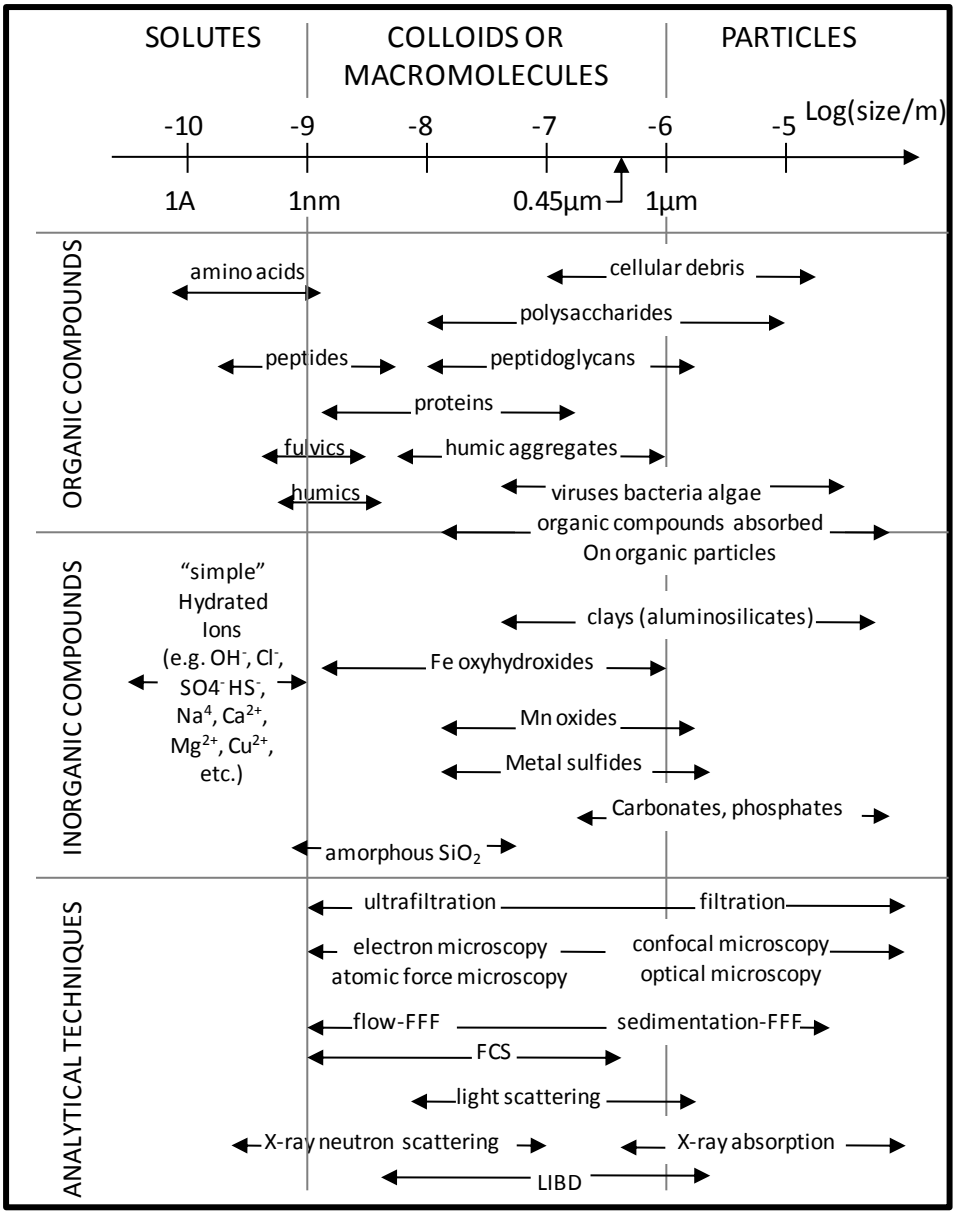


Figure 2.4 – Size range distribution (Ju-Nam and Lead, 2008)

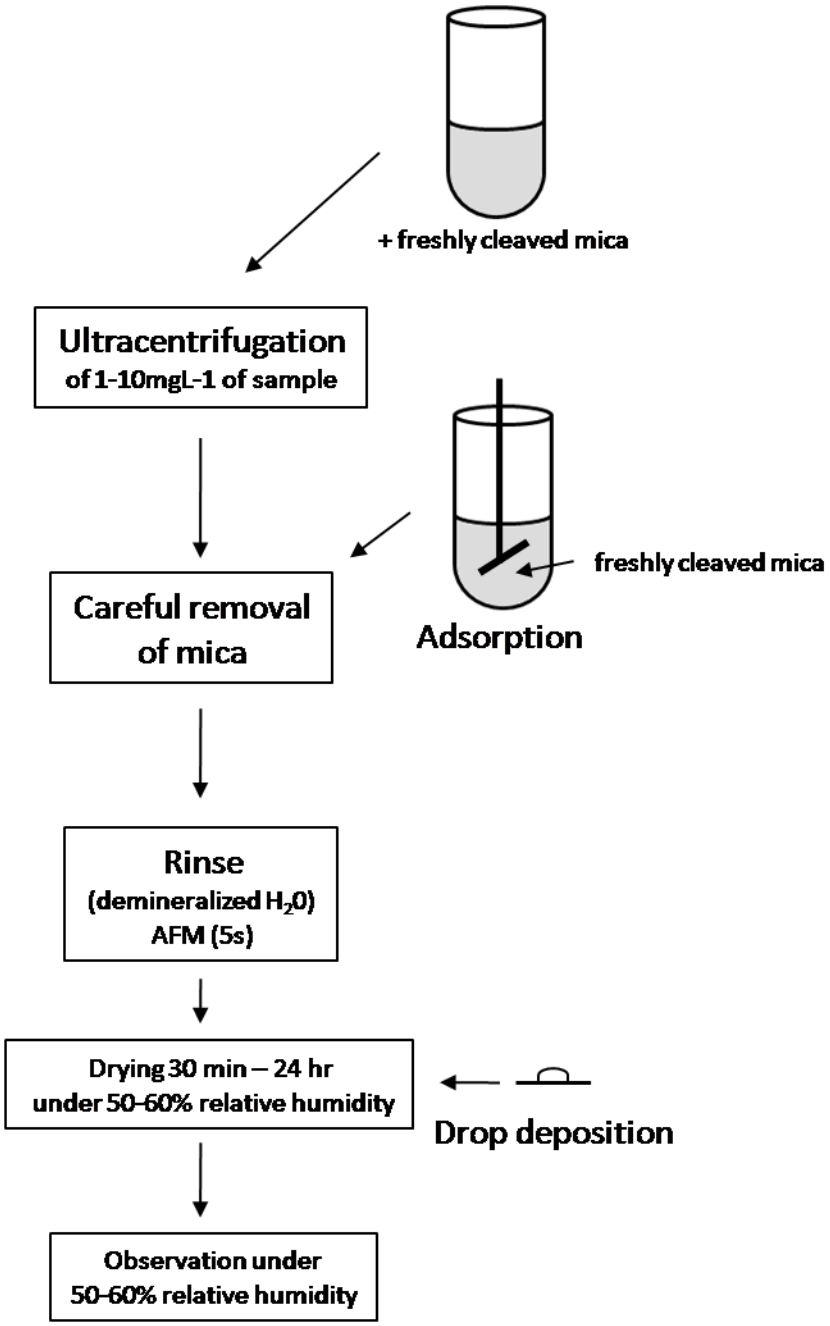


Figure 2.5 – Optimized sample preparation protocol for atomic force microscopy (AFM) (Wilkinson et al., 1999)

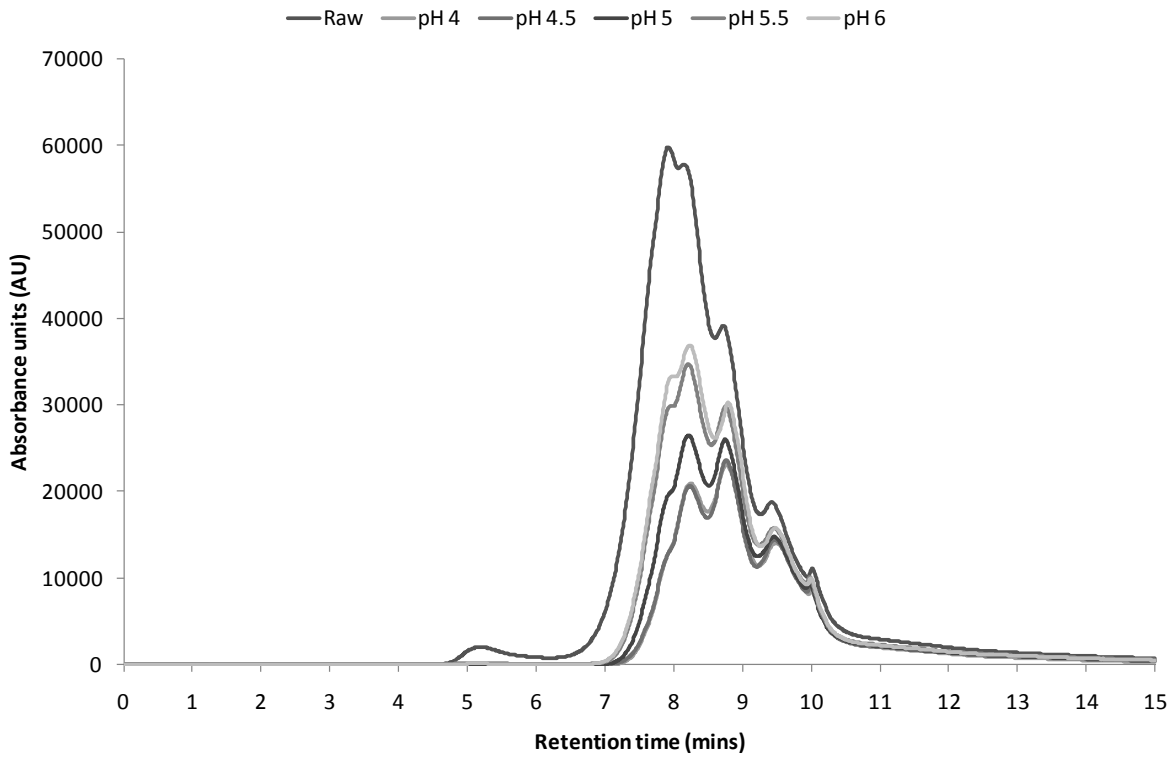


Figure 2.6 – HPSEC chromatogram for organics removal during pH range 4-6.

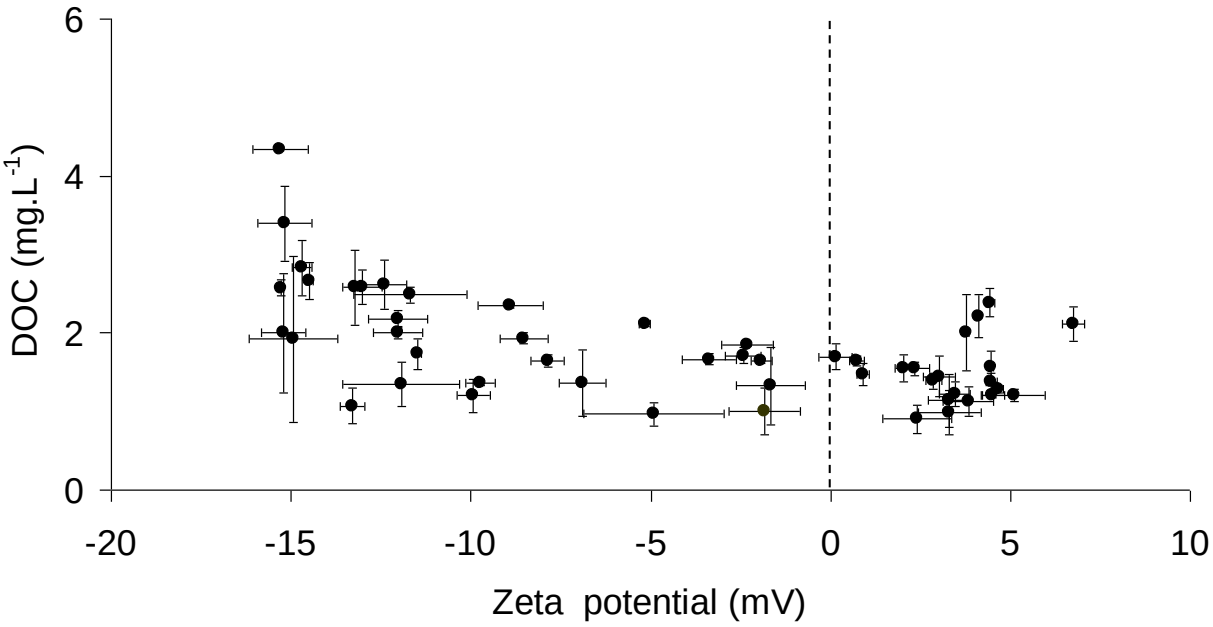


Figure 2.7 – Zeta potential Vs DOC residual (Sharp et al., 2005)

Chapter 2 Tables

Table 2.1 – NOM characterisation methods and their positives and negatives (adapted from Matilainen et al., (2001))

Characterisation Method	Example analysis tools	Features	Positives	Negatives
Preliminary Characterisation	TOC & DOC	Total organic carbon content in water & dissolved organic carbon in water (though 0.45µm filter)	Easy to use, analytical equipment not too expensive. Can be used as an on-line method.	Only gives quantity information.
	Ultraviolet absorbance (UV)	Quantitative measurement of all compounds in a sample that absorb UV light.	Simple and fast	Not all compounds are light absorbing. Method sensitive to chemical environment (e.g. pH and ionic strength)
Size Characterisation	HPSEC	Fractionates NOM on basis of molecular sizes of organic compounds present.	Rapid, sensitive, no pre-extraction required.	Charge effects during measurement (column/NOM, eluent/NOM), choice of detector and proper standards. Only usually available in laboratories.
Chemical Identification and behaviour	Resin fractionation	Isolates NOM fractions based on aromatic character.	Quick process and gives basic NOM character.	Needs to be combined with DOC, only gives quantity information and lab based process. Also, possible chemical or physical alterations to NOM.
	GC-MS	Structural and molecular properties of compounds in NOM.	Sensitive, specific, quick.	Unwanted thermal reactions. Data interpretation is difficult because of complexity of NOM.
	^{13}C NMR	Carboxylic structes of NOM.	Can be done on both solid or liquid sample, powerful characterisation tool.	Less sensitive to carbon than ^{1}H NOM to hydrogen. NOM sample needs to be isolated in solid state NMR measurements.
Spectral Signature	Fluorescence spectroscopy	Identifies NOM component based on particle wavelength.	Better sensitivity and selectivity than UV-vis, rapid analysis tool.	Requires data analysis, HPI signatures masked.

Table 2.2 – SUVA guidelines on nature of NOM and expected DOC removals (Edzwald and Tobiason, 1999)

SUVA ($L\ mg^{-1}\ m^{-1}$)	Composition	Coagulation	DOC Removal
> 4	Mostly aquatic humics, high hydrophobicity, high molecular weight	NOM controls, good DOC removal	> 50% for Alum, little greater for Ferric
2- 4	Mixture of aquatic humics and other NOM, mixture of hydrophobic and hydrophilic NOM, mixture of molecular weights	NOM influences, DOC removal should be fair to good	25-50% for Alum, little greater for Ferric
< 2	Mostly non-humics, low hydrophobicity, low molecular weight	NOM has little influence, poor DOC removal	< 25% for Alum, little greater for Ferric

Table 2.3 – Typical fluorescence peaks found in natural waters (Matilainen et al., 2011)

Range of excitation (nm)	Range of emission (nm)	Component type	References
270-280	310-320	Tyrosine-like, protein like	(Coble, 1996, Baghoth et al., 2009)
270-285 (220-235)	340-360	Tryptophan-like, protein like	(Coble, 1996, Baker et al., 2008, Spencer et al., 2007, Hudson et al., 2008)
320-350	400-450	Fulvic-like	(Spencer et al., 2007 Baker et al., 2009)
330-390	420-500	Humic-like	(Coble, 1996, Spencer et al., 2007, Baghoth et al., 2009)

Table 2.4 – Colloid and environmental nanoparticle analysis summary

	Analysis description	Best used for:
DLS	Measure of particle size and hydrodynamic diameter – how a particle diffuses within a liquid. Gives a measure of aggregation potential.	A rapid analysis tool that can give an indication of average particle size but not recommended for polydisperse samples. In water sample analysis, best used as a measure of ability to aggregate.
AFM	An imaging technique measuring minute forces when atoms or molecules interact, providing an image of the particle surface.	AFM imaging requires extensive sample preparation, however can provide detailed images of particle size and shape.
NTA	Particle size and number are determined using a laser light source to illuminate particles and measure using Brownian motion.	Requires limited sample preparation. Results prove particle distribution data, particle concentration data and drift velocities. Can also track particle movements in real time.

Table 2.5 – DBP produced in disinfection adapted from (Sadiq and Rodriguez, 2004)

Class of DBP	Common example	Chlorine	Ozone	ClO_2	Chloramines
Trihalomethanes (THM)	Chloroform	✓[a]	✓[b]		✓
Other haloalkanes		✓			
Haloalkenes		✓			
Haloacetic acids (HAA)	Chloroacetic acid	✓			✓
Haloaromatic acids		✓			
Other halomonocoarboxylic acids		✓			✓
Unsaturated halocarboxylic acids		✓			✓
Halodicarboxylic acid		✓			✓
Halotricarboxylic acid		✓			
MX and analogues		✓		✓	✓
Other halofurnaones		✓			
Haloketones		✓	✓	✓	
Haloacetonitrile (HAN)	Chloroacetonitrile	✓	✓		
Other halonitrile	Cyanogen chloride	✓			✓
Haloaldehyde	Choral hydrate	✓			✓
Haloalcohals		✓			✓
Phenols	2-Chlorophenol	✓	✓		
Halonitromethane	Chloropicrin	✓			
Inorganic compounds	Bromate, Hypobromite Chlorite and Chlorate etc.		✓	✓	
Aliphatic aldehyde	Formaldehyde	✓	✓	✓	
Other aldehydes		✓	✓	✓	
Ketones (aliphatic and aromatic)	Acetone	✓	✓	✓	
Carboxylic acids	Acetic acid	✓	✓	✓	
Aromatic acids	Benzoic acid	✓	✓	✓	
Aldo and Ketoacids			✓	✓	
Hydroxy acids		✓	✓		
Others		✓	✓	✓	✓

NB: Major classes of DBP are shown in bold

[a] There are four regulated THM compounds, but if iodomethanes are included in THM then there will be nine compounds

[b] Bromoform is produced if bromide ion is present

Table 2.6 – Summary of impact of water quality and treatment variables on THM and HAA formation. Adapted from (Amy et al., 2000, Bond et al., 2009, Bougeard et al., 2008, Brown, 2009)

Variable	Impact on THM	Impact on HAA
Contact time	Curvlinear increase with increasing contact time. Rapid formation < 5h. 90% formation in 24 h. Levels off at 96 h.	Curvinear increase with increasing contact time. Rapid formation < 5h. 90% formation in 24 h. Levels off at 150 h.
Disinfectant dose	Rapid and curvilinear increase after TOC demand with dose. Levels off at 2.0 mgL^{-1} for TOC of 2.0 mgL^{-1}.	Curvlinear increase after TOC demand with increasing dose. Levels off at 2.0 mgL^{-1}.
pH	Curvlinear increase with increasing pH to pH 7.0 and possible pH maximum. No positive effect at pH > 9.5.	Mixed, possible pH maximum for DCAA and DBAA. In lowland waters HAA levels decrease with increased pH.
Temperature	Linear increase with increasing temperature. (10-30 °C; 15-25% increase)	Increase with increasing temperature.
TOC	Increase with increasing TOC; precursor content important. Humic acids more reactive than fulvic acids.	Organic matter composition dependant, not overall TOC content.
UVA_{254}	Increase with increasing UV absorbance; precursor content important. Aromaticity of TOC being more important.	Limited correlation with UV, HAA formation correlated with HPI components (amino acids, aspartic acids and tryptophan) which are not identified by UV_{254}.
Bromide	Shift towards brominated species.	Shift towards brominated species, especially in upland waters
Alkalinity	No discernible effect.	No discernible effect.
Minimization strategies	TOC removal, minimizing chlorine residual, alternative disinfectants, pH control, minimizing contact time.	TOC removal, minimizing chlorine residual, alternative disinfectants, pH control, minimizing contact time.

Table 2.7 – UK and US THM and HAA regulatory limits and WHO guidelines (Richardson et al., 2007)

DBP	Drinking Water Inspectorate mgL^{-1}	EU Drinking Water Directive μgL^{-1}	US Environmental Protection Agency μgL^{-1}	US EPA Guidelines μgL^{-1}	WHO guidelines mgL^{-1}
TTHM	0.1	0.1	0.08		
Chloroform	n/a	n/a	n/a	0.07	0.20
Chlorodibromide	n/a	n/a	n/a	0.06	0.06
Bromodichloride	n/a	n/a	n/a	0	0.10
Bromoform	n/a	n/a	n/a	0	0.10
HAA_5	n/a	n/a	0.06		
Dichloroacetic acid	n/a	n/a	n/a	0.00	0.05
Trichloroacetic acid	n/a	n/a	n/a	0.02	0.02
Chloroacetic acid	n/a	n/a	n/a	0.07	n/a
Bromoacetic acid	n/a	n/a	n/a	0	n/a
Dibromoacetic acid	n/a	n/a	n/a	0	n/a
Bromate	n/a	0.01	0.01	0	0.01
Chlorite	n/a	n/a	1.0	80	0.7

Table 2.6 – Review of coagulants, adapted from (Matilainen et al., 2010, Duan and Gregory, 2003)

Chemical Class	Chemical	Advantages	Disadvantages
Hydrolyzing metal salts	Alum (Aluminium Sulphate)	• A standard in coagulation/flocculation. • Better turbidity removal than ferric. • Lower dose requirement and sludge produced.	• Fast mixing is critical to proper functioning. • Non-optimal pH leads to excessive dosage requirements and typically requires alkaline additives to achieve optimum pH. • Performance substantially degrades at lower temperatures. • Possible link to Alzheimer's disease.
	Ferric Chloride Ferric Sulphate	• Less sensitive to temperature than alum. • Gives more compact sludge. • Removal of middle-size not more effective than alum.	• Fast mixing critical to proper functioning. • Most effective at pH 4.5-6. • Sulphate and/or chloride in finished water increases corrosivity. • Typically requires alkaline additives to achieve optimum pH.
Pre-Hydrolyzed Metal Salts	PACl / PAC (Polyaluminium Chloride) Polyaliminium Sulfate	• Does not require addition of alkali to raw water for coagulation. • Much less sensitive to pH and temperature than alum and Ferric. • Less sludge produced.	• Generally requires an on-site production process to prepare pre-hydrolyzed metallic salts from alum. • Significantly affected by coagulant hydrolysis speciation.
	Polyiron Chloride	• Floc is tougher and larger. • Suitable for high colour applications.	• Generally requires an on-site production process to prepare pre-hydrolyzed metallic salts from chloride
Electrocoagulation		• Effective in all temperatures. • Removes smallest charge particles.	• Large amount of energy consumption which raises with NOM concentration.
Organic polyelectrolytes	PDADMAC CPAMs Chitosan	• Effectively targets HPO NOM. • Small amounts of sludge which is easier to dewater.	• High cost involved and toxic effects. • Forms smaller flocs
Anionic	APAMs	• Improved LMM removal.	• Not as effective as cationic polymers.

Chapter 3. Materials and methods

3.1 Sample sites

Severn Trent Water Ltd. (STW) is located in the Midlands region of the UK, covering approximately 20,720 square kilometres between the Humber and Severn estuaries supplying 1909 Mld of treated water to a population in excess of eight million. Figure 3.1 shows a map of the Severn Trent area and location of surface water sites. The majority of STW supply comes from 16 major surface water sites, although the company has an additional 180 groundwater abstraction sources. STW also imports upland water from the Elan Valley Reservoirs system in mid Wales. A gravity-fed aqueduct supplies 320 – 340 Mld to Site 6 WTW, supplying Birmingham, and if necessary, other supply zones using STW the strategic treated water grid, linking approximately 75% of STW consumers. Table 3.1 shows details of surface water site abstraction, treatment procedures and supply zones.

Surface water sites are located within the Severn and the Trent catchments. As raw water NOM is highly dependent on surrounding conditions, raw water profiles can vary extensively from site to site. Bieroza et al. (2009) compiled typical catchment characteristics for all 16 surface water sites (table 3.2) (Bieroza et al., 2009b). Typical land use patterns can be inferred from average site conditions as shown in table 3.3 obtained from Bieroza *et al.*, 2009b. For example, Site 1 WTW is dominated by pastures and upland peaty soils, which is illustrated by a high average UV of 29.42 and 35.69 abs m^{-1} of reservoir water, and a specific ultraviolet absorbance SUVA of 5.13 L mg^{-1} m^{-1}, indicating predominantly HPO NOM in soils.

In contrast, the Site 5 catchment has 65% non-irrigated arable land, with a corresponding lower UV of 12.15 m^{-1}, and SUVA of 2.25 L mg^{-1} m^{-1}, one of the lowest SUVA values of the 16 WTWs and indicating a dominance of HPI material in source waters.

An initial investigation into organic matter characteristics of all Severn Trent's sixteen surface water sites commenced in March 2006, with monthly analysis continuing until February 2008, providing an overview of organic character and treatability at all sites. Data analysis was initially performed by Severn Trent employee Emma Sharp, then by the author from October 2007. Data mining techniques were then employed to identify potential trends and relationships in the large dataset, which then led to the evaluation of low pH coagulation as a removal strategy. Subsequent research also focused on the investigation of two potential NOM characterisation methods, as limitations to existing NOM characterisation methods were identified by the initial investigation. Research following on from the initial 2 year investigation concentrated on a much smaller sampling area, namely five contrasting raw water profile surface water sites. Three sites were chosen due to their contrasting OM profiles; one with predominantly hydrophobic OM source water in an upland catchment (Site 1 WTW), one with predominantly hydrophilic OM source water in a lowland catchment (Site 5 WTW), and a site with OM characteristics falling between the two (Site 8 WTW). The final two sites (Site 13 and Site 16 WTWs) were chosen as existing Severn Trent taste and odour investigations were ongoing at these sites. These five sites are discussed in more detail below. Raw water characteristics for each are shown in table 3.3.

3.1.1 Site 1 WTW

Site 1 WTW is located towards the north east of the Peak District, and is one of Severn Trent's most northerly sites. Site 1 receives water from three reservoirs; Ladybower, Derwent and Howden. Site 1 has a distinctly rural setting, surrounded by large areas of open land belonging to the Peak District National Park and has many areas of farmland. The region is mountainous, with high levels of rainfall flowing through densely vegetated upland catchments, producing highly coloured source water. The works has a maximum capacity to treat 200 Mld, with the minimum at 90 Mld. Regularly dosing with lime to provide artificial alkalinity and precipitate calcium and magnesium ions, the water is coagulated with ferric sulphate and a dose of 9 mgl^{-1} is added. A Wispafloc A polymer is added before the precipitation tank. Raw water characteristics allow the highest average DOC removal rates of all the Severn Trent sites at 78.63%.

3.1.2 Site 5 WTW

Site 5 WTW is the most southerly of the selected sites and is situated between Coventry, Rugby and Leamington Spa. Water is abstracted from the River Avon, the Brownsover Pond and the River Leam and stored in a reservoir prior to treatment. The reservoir has a storage capacity of 23,000 Ml, indicating retention time is between 470-1270 days dependant on works output. The WTW supplies treated water to Coventry and Rugby. The catchment characteristics are typical of lowland areas. The WTW is immediately surrounded by some farmland and small towns and villages, with large towns in the distance.

The works has the capacity to treat between 18 and 50 Mld, and is one of the smaller works operated by Severn Trent. Treatment stages include straining, coagulation/flocculation,

clarification by dissolved air flotation (DAF), filtration, GAC and disinfection. Although source water is relatively colourless compared to other STW sites, a high proportion of recalcitrant hydrophilic OM in inlet water has a negative effect on overall DOC removal, with average removal at 18.52%. This is attributed to a typically lowland catchment dominant in HPI organic matter.

3.1.3 Site 8 WTW

Site 8 WTW is located in southern Derbyshire, near the Leicestershire border. The site abstracts from the River Dove at Egginton, some 2 miles from the WTW, just before the confluence with the River Trent. Site 8 stores raw water before treatment in the Staunton Harold or Foremark reservoirs with total raw water intake to the works from both reservoirs at 30% and 70% respectively. Resercoir levels are 13190 Ml for Foremark and 6655 Ml for Staunton Harold. At maximum output from the reservoirs, retention times are approximately 97 and 57 days for the Formark and Staunton Harold reservoirs respectively. Site 8 supplies the Hallgates and Ragdale segments of the STW distribution system, which in turn supply areas of Leicestershire.

Due to a predominantly rural surrounding area, raw water is usually coloured, but with a low turbidity. Maximum works capacity is 115 Mld from the Staunton Reservoir and 135 Mld from Foremark, with a minimum of 24 Mld and 60Ml.d respectively. Treatment comprises coagulation/flocculation, clarification (DAF), filtration, GAC and disinfection. The WTW uses ferric coagulant and achieves on average of 19.78% DOC removal through current coagulation conditions, however low pH coagulation has previously successfully

removed up to 68.34% DOC in the organic matter characterisation and low pH coagulation analysis performed between 2006 - 2008.

3.1.4 Site 13 WTW

Site 13 WTW abstracts directly from the River Severn (with no raw water storage), supplying parts of the Warwickshire and Coventry systems. The immediate surrounding area is arable and pastures, with few small rural towns. The M5 motorway runs through the catchment however, so is a potential source of diffuse pollution to the river and point sources from farming and industry may also influence raw water quality. Due to direct river abstraction, raw water quality is dependent on current climatic conditions and can exhibit extremes of turbidity, UV and DOC. The works treats an average 70 Mld, with maximum capacity at 160 Mld. Treatment processes at the works consist of screening, biological filters, coagulation, flocculation, clarification (hopper bottom clarifiers (HBC), filtration, (granular activated carbon (GAC) and disinfection. The works has the capability to switch between alum and ferric coagulants, although alum coagulation is predominantly used in order to prevent disruption to supply. Direct river abstraction, coupled with high turbidity in late summer and winter months mean average plant removal of DOC is 36.67%.

3.1.5 Site 16 WTW

Site 16 is located in North Warwickshire and is a relatively small capacity works. The works supplies the Nuneaton and Coventry areas from an on-site small capacity reservoir (24

hours retention time). The Rivers Bourne and Blythe supply the Upper and then Lower Shustoke reservoirs which is then fed to the works prior to treatment.

Raw water has high turbidity and UV, with a low SUVA rating of 2.45 L mg^{-1} m^{-1}, indicating a mixture of HPO and HPI organic material. Works capacity has an average output of 32 Mld and a maximum of 45 Mld. The treatment stages consist of coagulation/flocculation with Ferripol XL, a Fe^{3+} coagulant, clarification (HBC), filtration, GAC and disinfection. The works is also currently trialling coconut GAC media in one of its 16 vessels. The average percentage DOC removal for the works is 23.51%, reflective of the HPI content in raw waters.

3.2 Sample collection

Organics characterisation analysis of raw and clarified water samples from 16 surface water sites (19 source waters) were collected by an external contractor on a monthly basis between March 2006 and February 2008. Additional raw water samples were collected by the external contractor on a quarterly basis for more detailed characterisation studies, such as low pH coagulation and fractionation. For the monthly samples, 1 litre of raw and clarified water was collected, and 5 litres of the raw water were collected for the quarterly samples. Samples were collected in sterilised bottles and transported to the laboratory within 24 hours of collection, and stored in cool, dark conditions.

Site 13 WTW was identified as a site for further investigation from the organics characterisation investigation. In July, September and November 2008, 70 litres of raw

water were collected by the author on each sampling occasion in 5 L plastic bottles from the raw water inlet at the works. Specific dates were chosen in order to incorporate into the investigation the summer flush, occurring in approximately late August in 2008. Samples were transported to Severn Trent Laboratories (STL) in Coventry immediately for analysis and stored in cool, dry conditions before use (up to 2 weeks from sampling date).

The first stage of radiocarbon analysis commenced in June 2008. The second set of analyses commenced in July 2009, and finally the radiocarbon sterilisation investigation commenced sampling in October 2009 and continued on a weekly basis until late November 2009. This final set of sampling coincided with the colloids and environmental nanoparticles sampling. For all four investigations the sampling and transportation procedure was the same. Samples were collected in pre-acid washed 1 L PET bottles or 1 L glass schott bottles. Samples were then immediately transported to the University of Birmingham for analysis where they were stored in cool, dry conditions before use (maximum of 2 weeks).

Further information on sampling dates and measurements taken in each individual investigation is displayed in tables 3.4 – 3.9.

3.3 Bench scale jar tests

Quarterly organics characterisation investigations were carried out on all 16 surface water sites within Severn Trent. Raw waters from all surface water sites were coagulated at pH 4.5 using the current works coagulation dose. Research on optimal coagulation using zeta

potential measurements identified pH 4.5 as optimal for DOC, turbidity and UV_{254} removal (Sharp et al., 2006b).

Bench scale investigation into the effectiveness of low pH coagulation at Site 13 was undertaken in which a series of pH and coagulant doses were employed during the jar tests in order to simulate a range of THM reduction strategies. The performance of five different coagulant doses (2, 4, 6, 8, 10 $mg.l^{-1}$) was assessed at five pH values (4.0, 4.5, 5.0, 5.5, 6.0), making a total of 25 jar tests per sampling period. Sample numbers, pH and coagulant dose increments can be seen in table 3.5.

For each jar test, 2 litres of raw water were used to simulate coagulation and flocculation using a variable speed 2 blade impeller with square section, Phipps and Bird Jar tester. The jar testing procedure began with a 1.5 min rapid mix stage at 200 rotations per minute (rpm), at the start of which a set amount of Ferripol XL coagulant (a ferric coagulant in use on Severn Trent WTW sites) was added. During this stage, the pH was altered to the required value using 2 molar HCl and NaOH. 0.1 molar HCl and NaOH were also available for smaller pH adjustments. The rapid mix stage was followed by a 15 min slow mix stage at 30 rpm, at the start of which zeta potential measurements were taken. The jar tests were then left for a 20 min settling period, after which water quality (UV_{254}, NTU, DOC and HPSEC) and disinfection by-product (TTHM, THAAFP) measurements were taken.

3.4 Organic matter characterisation

3.4.1 DOC

Samples for DOC quantification were analysed using a PPM Labtoc Analyser, with a range of 0.18–10 mg.L^{-1} C. Samples were filtered though a 0.45 µm membrane prior to analysis. Samples were firstly mixed with persulphate, and inorganic carbon was purged off as CO_2. Samples were then swept by N_2 carrier to an Infra red detector to determine CO_2 at a wavelength of 4.4 µm, which was then related to the concentration of total carbon in sample. Accuracy and repeatability are ± 2 %.

3.4.2 UV_{254} and NTU

UV_{254} absorbance analysis was performed on the raw water and all jar tests after the 20 minute settling period, using a Biochrom Libra S12 spectrophotometer at a wavelength of 254 nm. Samples were filtered through a pre-rinsed 0.45 µm PALL filter papers and then analysed using a 1 cm quartz cuvette, rinsed with de-ionised (DI) water prior to each sample. For the Biochrom Libra S12 spectrophotometer at a wavelength of 254 nm, wavelength accuracy is ± 2 nm, with a photometric accuracy of ± 0.5 %.

For turbidity measurements, 30 ml of unfiltered sample was placed in a pre-rinsed vial and analysed using a 2100N Hach turbidimeter. A ± 2% accuracy of readings is used with Hach 2100N turbidimeters.

3.4.3 Fractionation

Raw water samples were characterised using fractionation techniques. Fractionation using XAD amberlite resins works by absorbing specific fractions in the water onto the resin, for example XAD-7HP resin absorbs hydrophobic material onto the resin, allowing quantification by DOC analysis on the remaining sample.

Samples were fractionated using Amberlite XAD-7HP and XAD-4 resins. As previously stated, XAD-7HP absorbs hydrophobic material with a moisture holding capacity of 61-69 %. XAD-4 resins absorb hydrophilic acids, leaving the hydrophilic neutrals and has a moisture holding capacity of 54-60 %. Resins were cleaned by pumping through 200 ml of 0.1 M NaOH. The resins were then primed with 200 ml of 0.1 M HCl, then 200 ml DI water. Prior to analysis, samples were filtered though a pre-rinsed 0.45 µm PALL filter papers and adjusted to pH 2 using 2 M and 0.1 M HCl. Samples were pumped through the resins, collected in 500 ml PET bottles and subsequently analysed for DOC concentration. Figure 3.2 illustrates the fractionation procedure and sampling points. Prior to DOC analysis, samples were stored in cool, dark conditions.

Using DOC results, fractions were calculated using:

HPO = Total DOC – HPI (sample point 2)

HPIA = HPI (sample point 2) – HPINA (sample point 3)

3.4.4 Zeta Potential

Zeta potential is a surrogate measurement for surface charge and is commonly used as a measure of coagulation performance. Coagulants coat particles, reducing electrostatic repulsion between particles and promoting binding formation of flocs. NOM removal conditions are thought to be optimal within a zeta potential range of -10 mV to +3 mV (Sharp et al., 2006b).

Zeta potential measurements were taken on the raw water, and also after 30 seconds of the slow mix stage in jar tests to provide an indication of coagulation performance. Zeta potential cells were rinsed with ethanol then DI water prior to usage. Samples were analysed in a zeta cell pre-rinsed with ethanol and de-ionised (DI) water, using a Malvern Nano-Z Zetasizer, with a ±1 % accuracy over the whole measurement range.

The Zetasizer Nano series calculates the zeta potential by determining the electrophoretic mobility and then applying the Henry equation:

$$U_E = \frac{2\varepsilon z f(ka)}{3\eta}$$

U_E = Electrophoretic mobility

ε = Dielectric constant

z = Zeta potential

η = Viscosity

f(ka) = Henrys function

Particles move towards the electrode of opposite charge, their velocity is measured and expressed in unit field strength as their mobility. The electrophoretic mobility is obtained by performing an electrophoresis experiment on the sample and measuring the velocity of the particles using laser Doppler velocimetry. Particles with zeta potentials more positive than +30 mV or more negative than -30 mV are normally considered stable in the absence of steric stabilisation.

3.4.5 Specific Ultraviolet Absorbance (SUVA)

$SUVA_{254}$, defined as the ratio of UV absorbance at a wavelength of 254 nm to the DOC concentration in mg L^{-1}, is used as an indicator of NOM character in a sample. It is especially useful in identifying the removal efficiency of specific NOM components (for example the hydrophilic content). $SUVA_{254}$ is calculated by dividing UV_{254} by DOC ($mg.L^{-1}$) and is expressed in L mg^{-1} m^{-1}. Table 3.10 details the significance of the calculated SUVA value. In 1999, Edzwald and Tobiason published guidelines for SUVA values, which have traditionally been attributed to NOM character and subsequent removal rates via traditional coagulation methods. Recent literature has highlighted concerns over the accuracy of $SUVA_{254}$ as an indicator of NOM content due to it being a measure of only the light-absorbing particles, which may not take into consideration potential DBP forming components that do not absorb light. Research has also indicated that observed relationships between $SUVA_{254}$ and DBP formation potential may be purely source water dependant (Ates et al., 2007a, A. et al., 2004).

3.4.6 High performance size exclusion chromatography (HPSEC)

HPSEC profiles are used to evaluate molecular sizes in samples, and show the size distribution of molecular weights. HPSEC is a well established form of NOM characterisation as when the sample traverses the column, the smaller compounds permeate the matrix pores to a greater extent than the larger compounds and are retained longer. Larger molecules are eluted from the column first, with the smaller molecules later. For each sample, a chromatogram of UV absorbance (absorbance units) against time (minutes) was produced. HPSEC analyses were performed at Cranfield University laboratories using a Shimadzu VP Series high performance liquid chromatograph (HPLC) with UV detection set to 254 nm, with a ± 1 % repeatability and accuracy. The column was a BIOSEP-SEC-S3000 7.8 mm (ID) x 30 cm, and the guard column was a 'security guard' fitted with a GFC-3000 disc 4.0 mm (ID) x 30 cm. Samples were filtered with pre-rinsed 0.45 µm PALL membranes before analysis at their natural DOC concentration. The HPLC mobile phase was 0.01 M sodium acetate at a flow rate of 1 $ml.min^{-1}$.

3.4.7 Fluorescence

Analyses were conducted using a Cary Eclipse Spectrophometer with a Peltier Temperature controller to maintain a constant 20°C during operation. The excitation wavelength was scanned in 5 nm increments from 200 to 400 nm, and the emission intensity from 280 to 500 nm. The recordings had a wavelength accuracy of ±1.5 nm, and a wavelength reproducibility of ± 0.2 nm. A raman peak intensity scan was conducted first for sample calibration, and fluorescence intensities recorded were subsequently corrected to a Raman

value of 20 units. No instrument specific corrections were carried out. All apparatus in contact with samples were rinsed with 0.1 M HCl and DI water.

The results are displayed in an excitation-emission matrix format (EEM), from which peak T intensity and peak C emission and intensity values were recorded. Peak T intensity is an indicator of the amino acid-like fraction and anthropogenic OM inputs (Bieroza et al., 2009b), with peaks occurring at an excitation wavelength of 280 nm and emission of 350 nm. Peak C is an indication of fulvic-like fluorescence material, with peaks occurring within a range of 300 – 340 nm excitation, 400 – 460 emission. An example of a typical raw water EEM with peaks identified is shown in figure 3.3.

3.5 Disinfection by-product formation analysis

3.5.1 Trihalomethane Formation Potential (THMFP)

THMFP measurements were performed at STL on all jar test waters and raw water using a HP6890 gas chromatograph fitted with electron capture detector (ECD). Samples were filtered though a pre-rinsed 0.45 µm PALL filter papers and transported in sealed 1 L green PET bottles. The samples were then buffered to pH 7 and spiked to approximately 5 $mg.L^{-1}$ free chlorine. Samples were then stored for seven days, with free chlorine levels checked after 3 days, with extra added if the chlorine level was found to drop below 0.5 $mg.L^{-1}$. 40 ml of the sample was then transferred to a septum vial left to equilibrate. After equilibration with the headspace at 80 °C, a sample of vapour was injected by autosampler onto a capillary column gas chromatograph.

3.5.2 Trihalomethanes (THM)

THM samples were also analysed using the HP6890 gas chromatograph with EDC fitting at STL, however, chlorine addition and fixing was performed prior to transfer to STL. Chlorine was added to a 40 ml sample from the jar test after the required settling period. Samples were then left for 40 minutes (to simulate a typical contact tank retention period) in sealed brown glass vials, then fixed with 0.7 ml of 70% sodium thiosulphate (supplied in analysis vials from STL). Samples were transferred to STL and analysed within 24 hours. As with THMFP analysis, samples were placed into a septum vial and allowed to equilibrate with the headspace vapour at 80 °C. Vapour was collected using an automatic headspace sampler and injected into the gas chromotgraph capillary column.

3.5.3 Haloacetic Acid Formation Potential (HAAFP)

HAAFP analyses were sub-contracted to Cranfield University and carried out using an Agilent 6890 gas chromatograph with micro electron capture. HAAFP analysis was carried out using a method adapted from method 5701B from The Standard Methods for the Examination of Water and Wastewater (18^{th} Edition, American Public Health Association 1992). Samples were filtered using pre-rinsed 0.45 µm PALL membranes then buffered at pH 7. Samples were then chlorinated with excess free chlorine at a ratio of 5:1 (chlorine:organic carbon) and stored at 20 °C for seven days. Samples were then injected to a capillary column with helium carrier gas at a constant rate of 1.1 mL min^{-1}, with an injector temperature of 200 °C and detector temperature at 230 °C.

3.6 Carbon isotope analysis

Radiocarbon isotope analysis was performed by the Natural Environment Research Council, Radiocarbon Facility (Environment) (NRCF(E)) in East Kilbride using the standard method for ^{14}C and ^{13}C abstraction and reporting (Craig, 1957, Stuiver and Polach, 1977).

Filtered samples were filtered through pre-combusted (4 hrs at 400ºC) 0.7µm GF/F glass microfibre filters. Inorganic carbon is removed from the samples via the process of acidification to pH4, which moves the bicarbonate equilibrium in favour of CO_2 formation, followed by nitrogen sparging to remove dissolved CO_2 from the sample. In the nitrogen sparging process, samples are adjusted to below pH 4 by dropwise addition of 2M HCl, then bottled nitrogen gas is bubbled through the sample for 30 minutes to ensure all CO_2 is evolved before the sample is neutralised to pH 7 by dropwise addition of 1M KOH. Unfiltered samples collected after GAC and disinfection treatment containing the 0.7 – 2 µm fraction due to previous filtering in the treatment process went straight to nitrogen sparging then rotary evaporation. Measured volumes of filtered sample were rotary evaporated (40°C; 50 mbar) in a Heidolph Rotary evaporator, Laborota 503 controller and water bath, until a few ml of solution remained. This concentrate was quantitatively transferred to pre-weighed, glass beakers and freeze-dried in a BOC Edwards freeze drier and the resultant solid homogenised. All glassware used in sample processing at the Natural Environment Research Council, Radiocarbon Facility (Environment) (NRCF(E)) was acid washed in (5M HNO_3) prior to use.

Resultant solids were weighed into 10x10mm tin capsules and combusted using a Costec ECS 4010 Elemental combustion system. The CO_2 generated was cryogenically purified and the volume recorded before the gas was collected in aliquots. One aliquot was converted to graphite by Fe/Zn reduction and the resultant graphite analysed for ^{14}C content at the Scottish Universities Environmental Research Centre (SUERC) AMS laboratory using a NEC 5MEV accelerator mass spectrometer (Xu et al., 2004). A further aliquot was analysed for $\delta^{13}C$ $‰_{V\text{-}PDB}$ using a dual inlet stable isotope mass spectrometer (VG OPTIMA). Isotope ratios were corrected using the procedure outlined by Craig (Craig, 1957) and are reported relative to the international reference standard Vienna Pee Dee Belemnite ($_{V\text{-}PDB}$) (Coplen, 1994). The recorded values for isotope standards are shown in table 3.11.

3.7 Colloids and environmental nanoparticles

Environmental nanoparticles analysis was performed by the NERC Facility for Environmental Nanoparticle Analysis and Characterisation (FENAC) based at the University of Birmingham.

3.7.1 Dynamic Light Scattering (DLS) and zeta potential

Particle sizes (hydrodynamic diameters), polydispersity index and zeta potential were all measured on a Zetasizer Nano ZS ZEN3600 (Malvern Instruments Ltd.) operating with a He-Ne laser at a wavelength of 633 nm using black scattered light. Measurement temperature was kept constant at 25 °C throughout the experiment. Results were the mean of ten measurements performed in each single run.

DLS is a non-invasive technique for characterising macromolecules in solution and particles in suspension. DLS measured the time-dependant fluctionations in the intensity of scattered light that occurs because the particles are undergoing random Brownian motion: the larger the particle, the slower the Brownian motion. A z-averaged translational diffusion coefficient D_Z can be determined from an autocorrelation of the Doppler shifts of the scattered light over time. This diffusion coefficient can be converted into a hydrodynamic diameter (D_H) using the Stokes-Einstein equation:

$$D = \frac{k_B T}{6\pi\eta r}$$

D = Diffusion Coefficient

k_B = Boltzmann Constant

T = Absolute temperature

η = Viscosity

r = Radius of a spherical particle

An accurately known temperature is necessary for DLS measurements since the temperature has a direct effect on the viscosity of the sample and hence the diffusion speed of the particles.

3.7.2 Nanoparticle Tracking Analysis (NTA)

Particle sizes and particle numbers were measured using a NanoSight LM10 system with a laser output of 30 mW at 650 nm. The instrument, which is based on a conventional optical

microscope, uses a laser light source to illuminate nano-scale particles within a 0.3 ml sample introduced to the viewing unit with a disposable syringe. Enhanced by a near perfect black background, particles appear individually as point scatters moving under Brownian motion. No sample preparation is needed prior to analysis.

Mean square displacements of single particles were determined by tracking the scattered light followed by analysis of the NTA software and standard deviations of the mean values were calculated. The NanoSight instrument tracks the Brownian motion of nanopartides in liquid suspension on a particle-by-particle basis. Subsequent application of the Stokes-Einstein equation allows the derivation of particle size and concentration. The mean squared distances that are travelled by the partides in two dimensions are recorded to determine number based diffusion coefficients.

3.7.3 Atomic Force Microscopy (AFM)

AFM is an imaging technique measuring minute forces when atoms or molecules interact. The principal part of the mechanical device called the cantilever is a plate spring, which is fixed at one end. At the other end it supports a pointed tip. The cantilever is typically silicon or silicon nitride with a tip radius of curvature of the order of nanometres. When the tip is brought into the proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Cantilever deflection is detected by a laser beam and movements of the reflected light are monitored by a photodiode detector. This information about the tip movement provides three-dimensional

images of the sample. In addition to imaging, the AFM can detect minute forces between the cantilever tip and a surface on a very fine spatial scale.

The adsorption method was used to prepare samples for AFM analysis, which preferentially investigates small particles, which are strongly sorbed to mica (Lead and Wilkinson, 2006). In this method, mica sheets were cleaved on both sides, then immersed vertically into the sample solution for 4 hrs. Following adsorption, the mica sheets were withdrawn from the solution and gently rinsed by immersion in deionised water to remove non-adsorbed sample. All AFM images were obtained using a XE-100 AFM (Park System). A Si non-contact mode tip with a force constant 42 (10 ~ 130) N m^{-1} (910M-NCHR) was employed. All scans were performed in air, at room temperature and AFM height measurements were recorded. For spherical particles, AFM height measurements will correspond to a number averaged diameter. Images were acquired in a true non-contact mode and recoded in topography mode with a pixel size of 256 x 256 and scan rate of 0.5 – 1.0 Hz.

3.7.4 Ultrafiltration

Separation of a range of species in different water samples were carried out by ultrafiltration. Samples were first filtered through a 0.1 µm filter and aliquots of the filtered sample were submitted to ultrafiltration through regenerated cellulose Ultracell YM Series membranes from Millipore Corporation with pore diameters of 1 nm under constant stirring.

3.7.5 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS is capable of the determination of a range of metals and several non-metals at concentrations below 10^{12}. Ionisation is performed by inductively coupled plasma, with a mass spectrometer to isolate and identify ions. ICP-MS is also used for the monitoring of isotopic speciation.

An Aligent 7500ce ICP-MS instrument with an Octopole Reaction System (ORS) was employed in the investigation. This system removes polyatomic interferences such as ArO, ArCl and Mar. Uniquely, the ORS removes interfaces independently of the analyte and sample matrix. This means that unknown samples can be analysed without requiring matrix specific or element-specific optimization, and without requiring any interference correction equations. The ICP-MS instrument uses ChemStation software for analysis.

Chapter 3 Figures

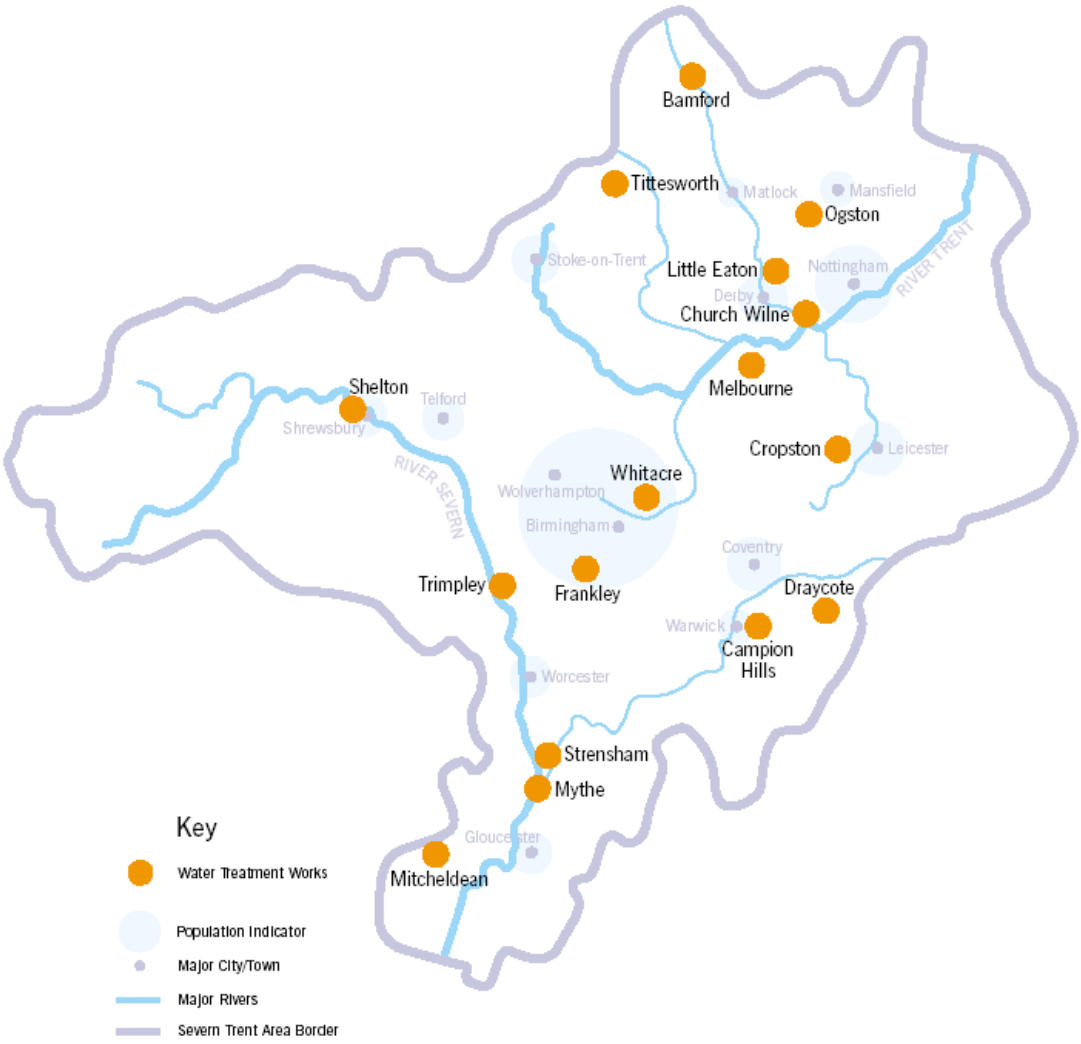


Figure 3.1 – Location of STW water treatment works (STW, 2010)

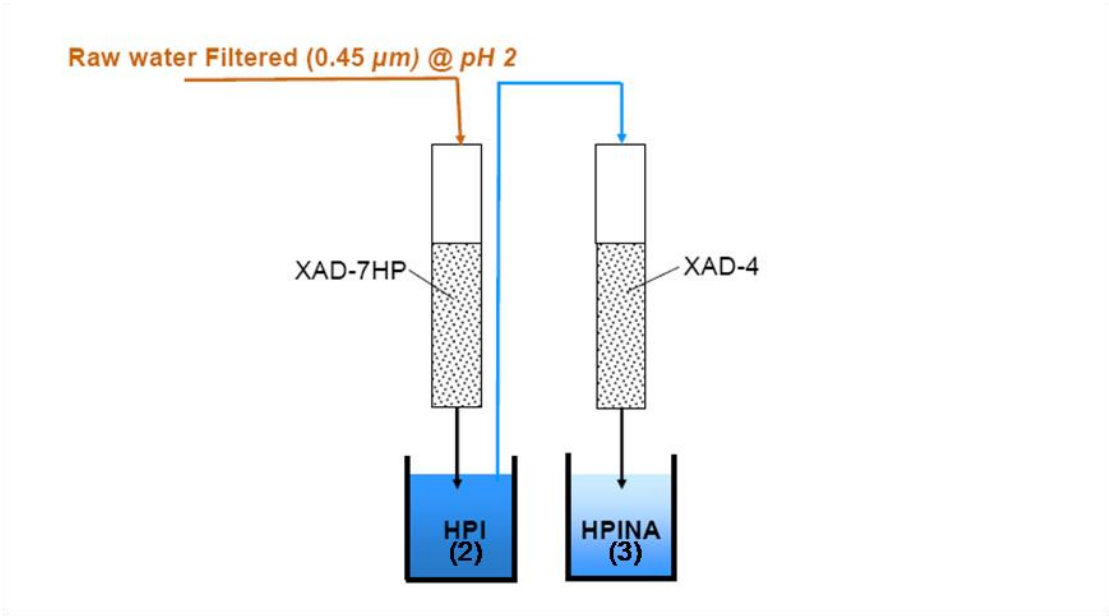


Figure 3.2 – Fractionation method

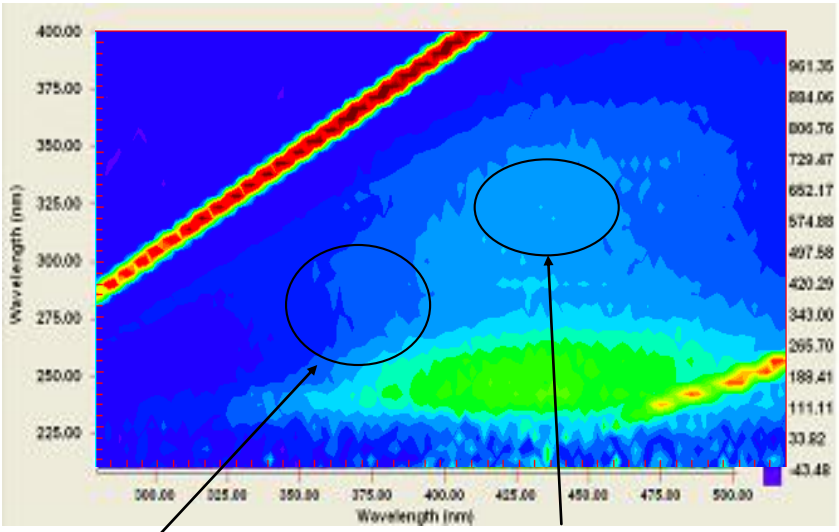


Figure 3.3 - Peak C and Peak T locations on an EEM

Chapter 3 Tables

Table 3.1 - Severn Trent sites information

Site	Abstraction Source	Works Capacity Min/Max (ML/D)	Coagulant (mgL^{-1})	pH Range	Clarification	Chlorine Dose (mgL^{-1})	Supply Zone
Site 1	Reservoir Source – LadyBower, Derwent & Howden	90/200	Ferric Sulphate ~6 mgL^{-1}	4.4 – 4.6	North: Precipitators South: HBC*	Up to 0.7	Gravity fed to DVA (Ambergate)
Site 2	River Leam	10/45	Ferric Chloride 6 – 8 mgL^{-1}	No Target	HBC	1.5 – 3	Leamington Spa
Site 3	River Derwent (Site 7 and Dracott Intake, River Trent (Witches Oak Intake)	20/135	Ferric Sulphate 5 – 8 mgL^{-1}		HBC (x16) DAF** (x5)		Hallgates, Strelley, Ratcliffe Power Station, Derby System.
Site 4	River Lyn	40 Max	Aluminium Sulphate 4.5 – 9 mgL^{-1}	6.2 – 8	DAF	1.3	Hallgates Service Reservoirs
Site 5	Rivers Avon & Leam, Brownsover Pond	18/50	Ferric Sulphate 6 – 8 mgL^{-1}	5 – 9	DAF	1.2	Coventry, Rugby & Barby
Site 6	Elan Valley	280/450	Ferric Sulphate 2.2 – 6.5 mgL^{-1}	5.2 – 6.4	DAF	1.01	Birmingham
Site 7	River Derwent	37/45	Ferripol XL (Ferric Sulphate) 8 – 16 mgL^{-1}	No Target	Lamella Plate Clarifiers	1.5	Radbourne/Drum Hill Reservoirs
Site 8	River Dove (Staunton & Foremark Reservoir)	Staunton H: 24/120 Foremark: 60/135	Ferripol XL (Ferric Sulphate) 2.4 – 12.8 mgL^{-1}	7 – 8	DAF	1.8	Smisby/ Hallgates & Ragdale Reservoirs
Site 9	River Wye	15/55	Ferripol XL 4 - 9 mgL^{-1}	5.5 – 8	HBC	1.2	Various Reservoirs, Stroud, Gloucester,

							Site 9 Town & Welsh Water
Site 10	River Severn	60-70/120	Aluminium Sulphate 1 – 6 mgL^{-1}	6 – 7.3	HBC & FBC***	2- 3	Cheltenham, Gloucester & Site 13
Site 11	River Derwent	45/90	Feripol 125S 6 – 10 mgL^{-1}	8 – 8.8	HBC (old works) DAF (new works	1.85	Big Higham Reservoir, Ambergate & Whiteborough
Site 12	River Severn	9/27	Aluminium Sulphate 1 – 6 mgL^{-1}	5.8 – 7.2	HBC	1 – 1.5	Shrewsbury
Site 13	River Severn (Upton Intake)	70/160	Aluminium Sulphate/Ferripol 1 – 6 mgL^{-1}	5.8 – 7.2 (Alum) 5 – 8.5 (Fe)	HBC	2.5	Meriden/Coventry, Worcester & Site 10 WTW
Site 14	Site 14 Res (River Churnet)	16/48	Ferripol XL 9.4 – 13 mgL^{-1}	5.5 – 6.2	DAF	1	Ladderedge, Kniveden
Site 15	River Severn	20/70	Ferripol XL 13 mgL^{-1} (DAF) 8 mgL^{-1} (HBC)	5 – 8.5	HBC, DAF	1.1	Ludlow/Shropshire, Site 15 Top,Worcester
Site 16	Rivers Bourne & Blythe	32/45	Ferripol XL 10 – 14 mgL^{-1}	5 – 9.0	HBC	2.0	Nuneaton, Coventry

* Hopper Bottomed Clarifiers (HBC) ** Dissolved Air Flotation (DAF) *** Flat Bottomed Clarifiers (FBC)

Table 3.2 – Summary of sample site catchment conditions (Bieroza et al. 2009)

Site	Catchment	Catchment area (sq km)	Source	Typical catchment land use (main divisions)
Site 1	Derwent to confluence with Wye	231.9	Reservoir	P 48%, O 39%
Site 2	River Leam	372.9	River	A 65%, P 25%
Site 3	Trent to confluence with Soar	7.2	River	P 44%, C 19%, U 11%
Site 4	Soar to confluence with Kingston Brook	283.2	River	A 48%, P 24%, U 11%
Site 5	River Leam	372.9	River	A 65%, P 25%
Site 6	Elan Valley	152.9	Reservoir	P 45%, A 33%
Site 7	Derwent to confluence with Markeaton Brook	15.8	River*	A 26%, U 21%, G 21%, P 21%
Site 8	Trent to confluence with Derwent	265.3	River	A 43%, P 30%, U 10%
Site 9	Lower Severn	844.4	River*	P 30%, A 26%, C 13%, F 11%
Site 10	Lower Avon	351.1	River*	A 63%, P 24%
Site 11	River Amber	145.1	River	P 55%, C 15%, A 11%, U 11%
Site 12	Upper Mid Severn	1161.5	River*	A 38%, P 31%, C 14%
Site 13	Lower Avon	351.1	River*	A 63%, P 24%
Site 14	River Churnet	231.7	Reservoir	A 76%, F 10%
Site 15	Upper Mid Severn	1161.5	River/Reservoir	A 38%, P 31%, C 14%
Site 16	Lower Blythe	0.9	River	A 55%, I 32%, F 13%

* - direct abstraction from river to WTW; Typical catchment land use, selected, types, of the largest percentage in total catchment area : A – non-irrigated arable land; P – pastures; C – other cultivated areas; U – urban fabric; I – industrial, transport or commercial units; G – green urban areas; F – forests; O – other areas.

Table 3.3 – Average raw water conditions, n = 447 (March 2006 – February 2008)

Site	pH	UV_{254} (abs m^{-1})	Turbidity (NTU)	DOC (mgl^{-1})	SUVA* (L mg^{-1} m^{-1})
Site 1 Raw 1	6.2	32.0	1.5	5.5	5.7
Site 1 Raw 3	6.1	38.3	1.7	6.7	5.5
Site 2	7.6	12.9	7.6	5.3	2.3
Site 3	7.6	8.9	1.4	3.1	2.7
Site 4	7.6	19.4	4.0	7.2	2.6
Site 5	7.9	12.2	1.1	5.9	2.3
Site 6	6.7	11.0	1.1	2.7	3.9
Site 7	7.5	8.9	3.9	2.9	2.8
Site 8 Reservoir SH	7.6	11.8	1.2	4.3	4.5
Site 8 Reservoir F	7.8	11.4	1.2	4.0	2.8
Site 9	7.4	8.7	3.5	2.8	2.9
Site 10	7.4	13.2	7.2	4.4	2.9
Site 11	7.6	13.1	1.6	4.7	2.7
Site 12	7.2	13.2	5.7	4.0	3.1
Site 13	7.4	14.6	6.9	4.3	3.2
Site 14	6.8	24.3	3.5	6.7	3.5
Site 15	7.4	14.8	3.1	4.5	3.1
Site 16	7.6	14.7	3.7	5.7	2.5

*SUVA – Specific UV Absorbance

Table 3.4 – NOM Characterisation sampling; March 2006 – February 2008

Parameter	Sample points(s)	Sampling duration	Total samples
Zeta potential*	Raw and final water.	Monthly	48
	Low pH jar tests.	Quarterly	8
UV_{254}*	Raw and final water.	Monthly	48
	Low pH jar tests.	Quarterly	8
Turbidity*	Raw and final water.	Monthly	48
	Low pH jar tests.	Quarterly	8
DOC	Raw and final water.	Monthly	48
	Low pH jar tests.	Quarterly	8
HPSEC	Raw and final water.	Monthly	48
	Low pH jar tests.	Quarterly	8
TTHMFP	Raw water and low pH jar tests.	Quarterly	16
THAAFP	Raw water and low pH jar tests.	Quarterly	16
Fractionation	Raw water and low pH jar tests.	Quarterly	16
SUVA	Raw and final water.	Monthly	48
	Low pH jar tests.	Quarterly	8
pH	Raw and final water.	Monthly	48
	Low pH jar tests.	Quarterly	8

*Triplicate measurements.

Table 3.5 – Site 13 low pH coagulation sampling; 25 low pH jar tests in each sampling period in July, September and November 2008

Parameter	Sample points(s)	Total samples
Zeta potential*	Raw water and 20 seconds into each low pH jar test.	78
UV_{254}*	Raw water and each low pH jar test after 20 minute settling period.	78
Turbidity*	Raw water and each low pH jar test after 20 minute settling period.	78
DOC	Raw water and each low pH jar test after 20 minute settling period.	78
HPSEC	Raw water and each low pH jar test after 20 minute settling period.	78
TTHMFP	Raw water and each low pH jar test after 20 minute settling period.	78
THAAFP	Raw water and each low pH jar test after 20 minute settling period.	78
Fractionation	Raw water.	3
Fluorescence**	Raw water and each low pH jar test after 20 minute settling period.	26
SUVA	Raw water and each low pH jar test after 20 minute settling period.	78
pH	Raw water and each low pH jar test in rapid mix stage.	78

*Triplicate measurements

**Fluorescence measurements taken only in November due to a later extension of project scope

Table 3.6 – NERC GAC investigation 1 sampling; July and November 2008, sites Site 13, Site 5, Site 3, Site 2, Site 8 and Site 16

Parameter	Sample points(s)	Total samples
Zeta potential*	Raw and P-GAC waters	24
UV_{254}*	Raw and P-GAC waters	24
TTHM**	P-GAC waters; time increments of 5, 15, 30, 60 and 120 minutes and a blank standard. 6 samples per site.	72
DOC	Raw and P-GAC waters	24
Fluorescence	Raw and P-GAC waters	24
Carbon isotopes ^{13}C and ^{14}C	P-GAC waters	10

*Triplicate measurements.
**Duplicate measurements

Table 3.7 – NERC P-GAC sampling 2; June 2009, sites Site 16 and Site 8

Parameter	Sample points(s)	Total samples
UV_{254}*	Raw water, post clarification, post filtration, post filtration unfiltered, P-GAC, P-GAC unfiltered.	14
Turbidity*	Raw water, post clarification, post filtration, post filtration unfiltered, P-GAC, P-GAC unfiltered.	14
DOC	Raw water, post clarification, post filtration, post filtration unfiltered, P-GAC, P-GAC unfiltered.	14
Carbon isotopes ^{13}C and ^{14}C	Raw water, post clarification, post filtration, post filtration unfiltered, P-GAC, P-GAC unfiltered.	14
TTHM**	Raw water, post clarification, post filtration, P-GAC. 30 and 60 minute time increments and blank samples.	24
Fluorescence**	Raw water, post clarification, post filtration, post filtration unfiltered, P-GAC, P-GAC unfiltered.	14
pH	Raw water, post clarification, post filtration, post filtration unfiltered, P-GAC, P-GAC unfiltered.	14

*Triplicate measurements.
**Duplicate measurements.

Table 3.8 – NERC Sterilisation investigation sampling; August 2009, sites 1, 8 and 16

Parameter	Sample points(s)	Total samples
UV_{254}*	Filtered, rolling boil and autoclave samples.	27
Turbidity*	Filtered samples.	9
TOC	Filtered, rolling boil and autoclave samples.	27
Carbon isotopes ^{13}C and ^{14}C	Filtered, rolling boil and autoclave samples.	27
TTHM**	Filtered samples, 30 and 60 minute increments.	18
Fluorescence**	Filtered, rolling boil and autoclave samples.	27
pH	Filtered samples.	9

*Triplicate measurements.
**Duplicate measurements.

Table 3.9 – FENAC colloids and environmental nanoparticles sampling; October 2009, sites 1, 5, 8, 13 and 16

Parameter	Sample points(s)	Total samples
UV_{254}*	1.00, 0.45, 0.22 and 0.10 µm size fractions for each raw water, post clarification, post filtration and post-GAC samples.	76
Turbidity*	1.00, 0.45, 0.22 and 0.10 µm size fractions for each raw water, post clarification, post filtration and post-GAC samples.	76
DOC	1.00, 0.45, 0.22 and 0.10 µm size fractions for each raw water, post clarification, post filtration and post-GAC samples.	76
TTHMFP	Raw and post-GAC waters.	20
TTHM**	Raw and post-GAC waters.	20
Fluorescence**	1.00, 0.45, 0.22 and 0.10 µm size fractions for each raw water, post clarification, post filtration and post-GAC samples.	76
pH	Raw water, post clarification, post filtration and post-GAC samples.	20
Fractionation	Raw and post-GAC waters.	20
Zeta Potential	0.10 µm size fractions for each raw water, post clarification, post filtration and post-GAC samples.	20
ICP-MS	0.10 µm size fractions for each raw water, post clarification, post filtration and post-GAC samples.	20
DLS	0.10 µm size fractions for each raw water, post clarification, post filtration and post-GAC samples.	20
AFM	0.10 µm size fractions for each raw water, post clarification, post filtration and post-GAC samples.	20

*Triplicate measurements.
**Duplicate measurements.

Table 3.10 – SUVA guidelines on nature of NOM and expected DOC removals (Edzwald and Tobiason, 1999)

SUVA ($L\ mg^{-1}\ m^{-1}$)	Composition	Coagulation	DOC Removal
> 4	Mostly aquatic humics, high hydrophobicity, high molecular weight	NOM controls, good DOC removal	> 50% for Alum, little greater for Ferric
2- 4	Mixture of aquatic humics and other NOM, mixture of hydrophobic and hydrophilic NOM, mixture of molecular weights	NOM influences, DOC removal should be fair to good	25-50% for Alum, little greater for Ferric
< 2	Mostly non-humics, low hydrophobicity, low molecular weight	NOM has little influence, poor DOC removal	< 25% for Alum, little greater for Ferric

Table 3.11 – Carbon isotope standards

Sample	^{14}C (%mc)	Conventional radiocarbon age (years)	$\delta^{13}C$ (‰)
Heidelberg Wood	3.34 ± 0.05	27241.09	-19.82
Heidelberg Wood	0.26 ± 0.02	47722.22	-19.84
Heidelberg Wood	0.16 ± 0.01	51516.10	-20.20
Iceland Spar Calcite	0.13 ± 0.01	53633.48	2.38
Humin	65.27 ± 0.30	3369.23	-28.20
Humin	65.65 ± 0.31	3323.53	-27.33
Humin	65.29 ± 0.29	3367.76	-29.30
Barleymash	115.90 ± 0.51	modern	-26.87
Barleymash	116.01 ± 0.51	modern	-26.58

Chapter 4. NOM characterisation of surface water sites

4.1 Introduction

The presence of NOM in surface waters has been proven to negatively impact on the water treatment processes, especially coagulation and flocculation. Research into the characterisation of NOM could aid the removal of NOM in water treatment and reduce the formation of DBPs after disinfection and through distribution systems.

The work in this chapter focuses on objectives (i):

To evaluate the use of existing characterisation methods for the investigation of NOM composition and in the identification of key trends in NOM character, existing and achievable removal and DBP formation.

In particular, the work in this chapter focuses on the following research questions;

- Can existing NOM characterisation techniques be used to distinguish between surface water sites in the Severn Trent region?
- Can existing NOM characterisation parameters provide an insight into coagulation and clarification performance at Severn Trent surface water sites?
- Can existing NOM characterisation parameters identify a link between NOM composition and optimal removal of DOC at the respective sites?
- Can existing characterisation methods identify a link between NOM composition and THM and HAA formation potential at Severn Trent surface water sites?

In order to address these objectives and research questions, raw and clarified samples from sixteen surface water treatment sites in the Severn Trent region were examined. Samples were collected by an external contractor on a monthly basis in order to quantify the source water characteristics and monitor current plant performance of organics removal. Additional raw water samples were taken on a quarterly basis for more detailed characterisation studies. Sample collection started in March 2006 and continued until February 2008.

For the monthly samples, one litre from both raw and clarified outlets were collected. Five litres of the raw water were collected for quarterly samples. Samples were collected and transported to the laboratory within 24 hours of collection.

4.2 Source water characterisation

Average DOC over the two years ranged from 2.68 $mg.l^{-1}$ at Site 6's Site 6 Reservoir to 7.15 $mg.l^{-1}$ at Site 4 (table 4.1). Sites typically high in colour, such as Site 1 (Ladybower and Derwent reservoirs), although not having the highest DOC amounts (5.51 $mg.L^{-1}$ for Site 1 Ladybower, 6.73 $mg.L^{-1}$ at Site 1 Derwent) have consistently the highest SUVA score. When both raw water sources are combined, they give an average of 5.12 L mg^{-1} m^{-1}. This indicates the raw waters have a large average loading of HPO material, which is representative of a moorland catchment. When compared to sites with lowland water sources, such as Site 5, Site 16 and Site 2, SUVA values lie within the ranges 2.25-2.45 L mg^{-1} m^{-1}, indicating the presence of a greater percentage of non-charged HPI organics.

Due to the number of sites, for the purpose of this chapter only Site 1, Site 5 and Site 13 will be considered in detail. Site 1 and Site 5 are at either end of the SUVA scale and Site 13 is closest to the average SUVA for all sites.

SUVA profiles over the two year period shown in figure 4.1 compare the variation in NOM characteristics between the three sites. The typically lowland site, Site 5, has minimal variation in NOM composition over the range of the study. A high variance over the period was observed with the Site 13 SUVA profile, however this is to be expected from a direct river abstraction site. Interestingly, SUVA profiles for all three sites show very little discernable seasonal trends in HPI content that are frequently reported in scientific literature (Scott et al., 2001, Sharp et al., 2006e). Increases in the HPO materials are in the latter months of the year instead, in the late autumn/winter periods.

Raw water HPSEC profiles (figure 4.2) highlight the differences between the source water at the three sites, and indicate potential NOM profiles. Raw water at both Site 1 reservoirs are typically characterised by the occurrence of two distinct peaks. Although there is a wide range of organic material visible within the sample, the locations of these two peaks, and the size of the peak which indicates the concentration of each molecule size, indicates a water which is HPO rich. The complete absence of these two peaks in the site 5 sample indicates a lack of HPO material present. Also, as the first peak occurs after an elution time of nine minutes this indicates a dominance of smaller material, which is less likely to be HPO, and more HPI material (Goslan, 2003). Site 13 tends to mirror the Site 5 HPSEC profile, but shows a decreased total amount of organic material in total however there is a slight peak after an elution time of six minutes, indicating a small amount of HPO material.

Indications made by HPSEC analysis can be verified by fractionation data. Figure 4.3 shows that Site 1 combined raw waters are shown to be predominantly HPO organics. Over the two year period HPO material varies from 52 to 81% of the total DOC. It is not until July 2007, when the summer flooding occurred that HPI material makes up more than 40% of the total DOC load. Up until this point, the Site 1 fractionation data shows an excellent example of a typical autumn flush, bringing a greater amount of predominantly HPO DOC after periods of hot and dry weather followed by intense rainfall. In comparison, Site 5 HPI content varies from 45-74% over the two year period (figure 4.4). It also shows little variation throughout the year. This predominance of the more recalcitrant HPI material confirms the HPSEC findings and highlights the differences between the moorland and lowland source material. Site 13 fractionation data (figure 4.5) shows some variation over the quarterly periods, however the HPI/HPO split remains fairly constant at 55% HPO, 45% HPI.

A large increase in overall DOC concentration was however observed in Site 13 waters in July 2007 (figure 4.5), this is attributable to a series of high intensity rainfall events which is normally uncommon at this time of year. Fractionation data shows the organic character remains relatively unchanged although a slight reduction in the HPIA content of raw waters was observed (26.64% of total DOC in April 2007, reducing to 22.41% of total DOC in July 2007), a trend repeated in the remaining two sampling periods. Such increases in the overall content of NOM in surface waters was not evident at all three sites however, which is most likely to the reservoir storage at Site 1 and Site 5 acting as a buffer. Although an increase in the total amount of DOC is not evident, all three sites exhibit an increase in

HPINA content of NOM. An increase in the HPI content of raw waters has previously been reported in scientific literature, but the increase in HPIA NOM was not observed until the October. This could indicate that the HPINA content of NOM composition increases in the earlier summer months, however the HPIA content of NOM composition will not increase until the early autumn.

4.3 Current plant performance

Analysis of average plant performance during the sampling period (shown in table 4.2 demonstrated that Site 1 achieved very high removal rates of DOC between 74-83%, with an average removal of 78.61%. The lowland sites, particularly Site 5 only achieves limited average removal of DOC of 18.52% with a range of 9-30% over the two year investigation. Site 13 does have slightly better average removal rates of 36.09%. Removal ranges from 24-54% over the two year period however, resulting in frequent organic material residual with the potential to cause high DBP formation. Examination of the HPSEC profiles for each site, (figure 4.6 Site 1, figure 4.7 Site 5, figure 4.8 Site 13) shows the larger material, which are absorbed first onto the membrane, are removed more readily during treatment leaving predominantly the smaller HPI material, which is eluted after approximately nine minutes. It is the residual smaller molecular-sized material present after treatment at all three sites which indicate that the HPI material, with little or negligible charge density, is less susceptible to removal through current coagulation conditions. Additionally, Site 1 operates at a much lower pH, typically around 4.5, than the two lowland sites. As discussed previously, this could be a contributing factor to poorer removal rates in the latter cases.

4.4 Achievable NOM removal

Quarterly jar tests were employed to investigate optimal NOM removal with the reduction of coagulation pH. pHs were reduced to approximately 4.5 and current plant coagulant doses were used in order to minimise the number of changed variables. As Site 1 WTW currently operates at a lower pH than most sites, figure 4.9 shows that there are few distinguishable variations between the low pH jar tests and plant performance. Both produce consistent removal rates of 60-85%. Lowering coagulation pH could be beneficial if the WTW was experiencing difficulties with NOM removal, but it is unlikely pH alteration will contribute any further to removal rates with typical works performance.

Figure 4.10 shows that Site 5 WTW does not remove more than 30% of total DOC at current plant performance. Low pH jar tests show removal rates of 50-60% are achievable, however there is an overlap between low pH and average plant removal in some results as in October 2007 and January 2008, Site 5 suffered particularly poor percentage DOC removal, most likely due to the high HPIA content in source waters at this time.

Site 13 raw waters responded positively to low pH coagulation (figure 4.11), however an operational window of 5-5.5 would be recommended as below pH 5, low pH coagulation appeared to have detrimental effects on percentage DOC removal. Both lowland sources do, to an extent, demonstrate the advantages of low pH coagulation, but it is unlikely to be the main contributing factor for improved coagulation performance as substantial variation in percentage DOC removal is observed over a limited pH range. At lowland sites, the dominance of HPINA in source water composition is preventing increased removal with low

pH coagulation and would ultimately require investigation into alternative removal methods.

4.5 THM and HAA formation potential

THMFP was calculated for the raw source waters and the low pH coagulation jar test waters. Over the 2 year period, Site 1 source waters shown in figures 4.12 and 4.13 consistently have the highest THMFP from raw waters, however 82-92% of THMFP is successfully removed during low pH coagulation. Site 5 water shown in figure 4.14, is a typical lowland WTW with highly HPI source waters, is only able to remove 40-55% of total THMFP in low pH conditions. Site 13 waters (figure 4.15) do remove amounts as high as 81%, but removal was also reduced to 13% in low pH jar tests, which is possibly indicative of direct abstraction as the raw water quality is affected by antecedent rainfall. In addition, Site 13 is affected by regulation releases from Clywedog reservoir, resulting in an influx of organic material from an upland catchment, unlike what is typical for Site 13 WTW. The low 13% THMFP removal occurred in January 2008, which coincided with a lower coagulation pH of 4.5. Site 13 also experiences an influx of bromoform formation after low pH coagulation compared with existing treatment practices. This variation could be attributed to the reduction of pH having an effect on the bromide to NOM ratio. A study of the bromine incorporation factor by Rathbrun (1996) indicated that treatment conditions designed to minimize the total THM concentration (via organics removal) will most likely increase the extent of bromination. This could therefore be an implication on low pH coagulation that WTW would need to be wary of, especially considering brominated by-products are said to be more harmful than chlorinated by-products (Bull et al., 1991, Bove et al., 2007). This trend is also repeated with

Site 5 low pH THMFP, where levels of bromoform increase significantly after low pH jar tests.

This is not replicated at Site 1 or Site 5 which suggests direct river abstraction works could be susceptible to increased bromoform formation with low pH treatment. Moorland sources with increased loads of HPO material routinely have initial increased THMFP, however as this fraction is more readily removed during treatment they also exhibit greater removal of THMFPs such as chloroform. Lowland sources with predominantly HPI material present exhibit less original THMFP however, as these fractions are difficult to remove during treatment, they pose the greater risk with THMFP after chlorination and during distribution.

HAAFPs were also calculated on the raw source waters and the low pH coagulation jar test waters. Site 1 HAAFPs with low pH coagulation routinely achieve removal percentages of between 80-90%. Figure 4.16 shows that July and October months in 2006 only achieved 47% and 57% removal of total HAAFP with low pH coagulation, which could be attributed to the increased levels of low molecular weight, recalcitrant HPI material. This is mirrored by the decreased removal levels of total DOC that occurred on site and in low pH jar tests at this time. Site 5 HAAFP (figure 4.17) start with much lower amounts of total HAAFP in raw waters than in Site 1 waters. Removal percentages in low pH jar tests however are much more varied. Removals of 66% were achieved in April 2007, however as only 30 HAAFP/DOC µg.mg C was removed from the raw water, overall removals are still low in respect to Site 1, which regularly achieves up to 200 HAAFP/DOC µg.mgC removal. It is also worth noting that July and October 2006 HAAFP for low pH jar tests were greater than initial raw water HAAFP

levels. Site 13, as mixed HPI/HPO source water, exhibits removals of up to 90%, but also lows of 12%. The data indicates that, across all sites, low pH coagulation yields an average reduction of raw water HAAFP of 53%. Figure 4.18 shows that Site 13 HAAFP levels are higher than Site 5 waters but they are much more influenced by seasonal variations. October and January generally have higher levels of total HAAFP/DOC µg.mg C in raw waters, however removals for these months only range between 48-63%.

Links between NOM composition and DBP formation potential indicate an increase in brominated DBP formation at lowland sites. Site 5 has consistently higher levels of HPI NOM, particularly HPIA, which when coagulated at a low pH, the formation of brominated THMs increases. This suggests that lowland sites will need to have THM reduction strategies directed towards the removal of brominated THM species – which considering the dominance of chlorinated THM species at upland WTW, such treatment strategies would not be applicable at all works.

Further impacts of NOM character on DBP formation can be seen by the large increase in the HPINA component of NOM in July 2007 samples at Site 13. The increase in HPINA appears to have had a positive impact on THMFP, particularly chlorodibromide formation potential, where levels were lower than those recorded the year previously, and similar to the January THMFP levels. The increase of HPINA in raw waters had the greatest impact on HAAFP. At all three sites, levels of HAAFP were minimal in raw waters, and completely removed after treatment. Interestingly, a decrease in HPINA at Site 13 WTW in January 2006 and January 2007 coincided with a higher HAAFP of raw waters.

4.6 Discussion

Results from this investigation reveal that sites with a HPO content, for example moorland sources such as Site 1, are more susceptible to seasonal variations in organics concentration and composition. Lowland sources such as Site 5 do not experience such variation as HPI contents remain stable throughout the year. However, in extreme conditions, such as the June/July 2007 flooding, significant increases in NOM were recorded with the majority consisting of the HPO fraction.These results contradict published studies by Scott et al., (2001) and Sharp et al., (2006) which noted an increase in the HPI content of NOM in the summer months. At all three sites, an increase in HPI content was not observed until the October fractionation samples. Fractionation techniques were employed in both the aforementioned studies, so a lack of HPI bonding to resins cannot account for this difference. The Increased HPINA content of waters after the 2007 flood events in July suggest that the formation of HPI NOM is occurring in these summer months, but not typically being transported to the catchment until more intense or prolonged rainfall occurs. This suggests the formation of HPI NOM could be from material which is derived from the soil profile. Resin fractionation results were therefore able to demonstrate the changes in NOM composition over a specific time period, and allowed more insight into NOM composition than SUVA or DOC results. Poor HPI adsorption has previously been reported in scientific literature (Bond et al., 2009), as with concerns over physical alterations of NOM due to the low pH used to adhere particles to resins (Matilainen et al., 2010, Croué et al., 2000). In this study there appeared to be a direct comparison between resin fractionation profiles and SUVA results, however it is worth noting that methods used in the study would not be capable of identifying loses of NOM through resin fractionation.

HPSEC profiles demonstrated the capacity of coagulation and clarification for NOM removal at all three sites. It identified that sites with a high HPO were more amenable to removal by existing treatment methods, which is frequently reported in scientific literature (Fearing et al., 2004, Sharp et al., 2006a). HPSEC also identified the molecular weight of fractions that were least amenable to removal, and a by what quantity.

NOM characterisation methods also ascertained that current coagulation conditions at the majority of sites are unsuitable for the removal of high HPI waters. Treatment of surface waters using trivalent metal salts such as ferric chloride and aluminium sulphate are commonly used in the water industry (Matilainen et al., 2010, Duan and Gregory, 2003), however this study agrees with findings by Szlachta and Adamski (2009), Fabris et al., (2008) and Sharp et al., (2006a) that such coagulation mechanisms are inadequate for the removal of HPI NOM, and the HPI content is a good indicator for the residual DOC concentration. Sites such as Site 13, Site 5 and Site 2 are unable to remove sufficient organics on a everyday basis and would benefit from optimised NOM removal strategies, as current coagulation pHs between 7.2-7.8 are too high throughout the year. Results also showed that low pH coagulation was able to increase removal at Site 5 from 10-30% to 50-60%, which could be increased further with investigation into optimal coagulant dose. pH reduction did have a significant impact on NOM removal at all size fractions, however optimal pH is dependent on source type (Jarvis et al, 2008) as even at such a low pH, coagulation was unable to remove a majority of the HPI NOM. Results also showed significant variation in total DOC removal at similar pHs, demonstrating that pH is not the main influential factor when removing organics.

THMFP and HAAFP results provided little insight into seasonal variation at the three sites. The most notable results were with the increase in HPINA in July 2007 and the impact this had on DBP formation, particularly HAAFP, confirming research by Goslan et al., (2009) and Bond et al., (2009) showing that HAAFP had little link to THMFP. Results also agreed with DWI (2009) findings that HAA levels were greater in autumn months. The effect of an increase in HPINA has not previously been reported about in scientific literature, however Bond et al., (2009) and Reckhow and Kim (2008) did conclude that the HAAFP of HPI compounds were found to increase after treatment, so the reduction in HPIA seen in July 2007 could be a factor contributing to this.

The increased levels of brominated DBP formed at Site 5 could also be linked to the contrasting NOM characteristics found between the sites. Low pH coagulation at Site 5 had a significant effect on the production of brominated DBP, which as previously discussed could be due to the bromine incorporation factor (Rathburn et al., 1996). This implies that if DBP reduction strategies were to be employed at WTW that lowland sites would be at risk if significantly increasing brominated DBP formation.

4.7 Conclusions

In conclusion, NOM characterisation techniques were able to identify significant variation in NOM composition between sites. UV and SUVA methods were best employed for an overview of NOM character, however resin fractionation and especially HPSEC would need to be used for a detailed insight. HPSEC was the most relevant technique for identifying

coagulation and clarification performance, and the impact of low pH coagulation on the various NOM MW.

Optimal DOC removal was at the HPO dominated sites, however the study did highlight that if low pH coagulation were to be employed at a lowland site such as Site 5, it would be at risk of increasing the formation of brominated DBP and therefore have little reduction on DBP formation. Sites with a high overall HPI content of NOM would therefore benefit from investigation into additional removal technologies and coagulation supplements.

A potential link between NOM character and DBP formation was identified with a decrease in HPINA content having a positive impact on DBP formation. It was also noted that HPINA NOM had a considerable potential to form DBP.

Existing NOM characterisation techniques were therefore able to distinguish between NOM composition at WTW, however they had limited effect with identifying links between NOM composition and DBP formation potential.

Chapter 4 Figures

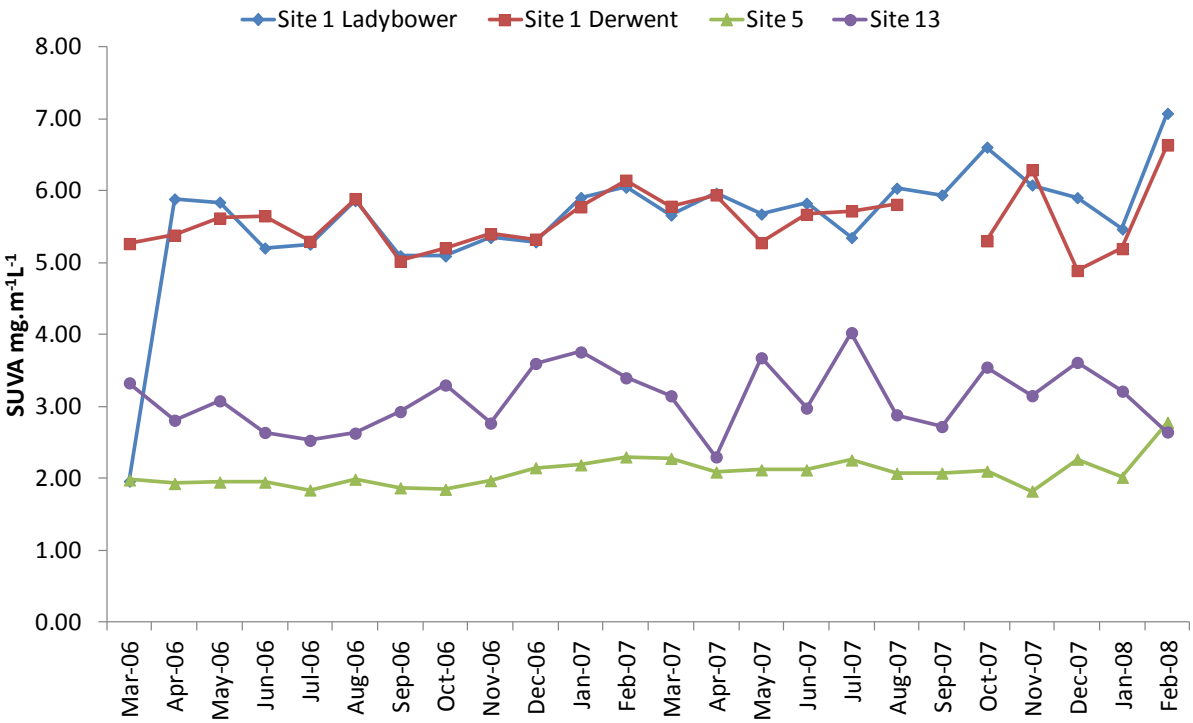


Figure 4.1 – SUVA profiles over sampling period

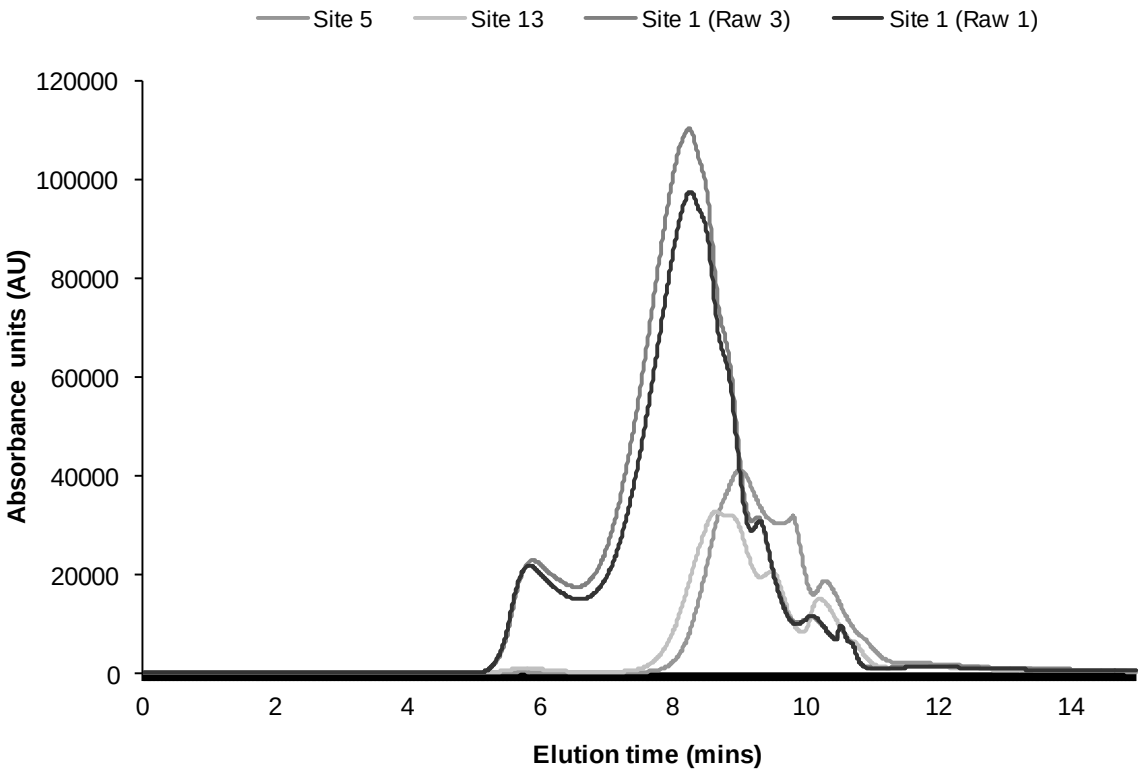


Figure 4.2 – Raw water HPSEC chromatogram (January 2008)

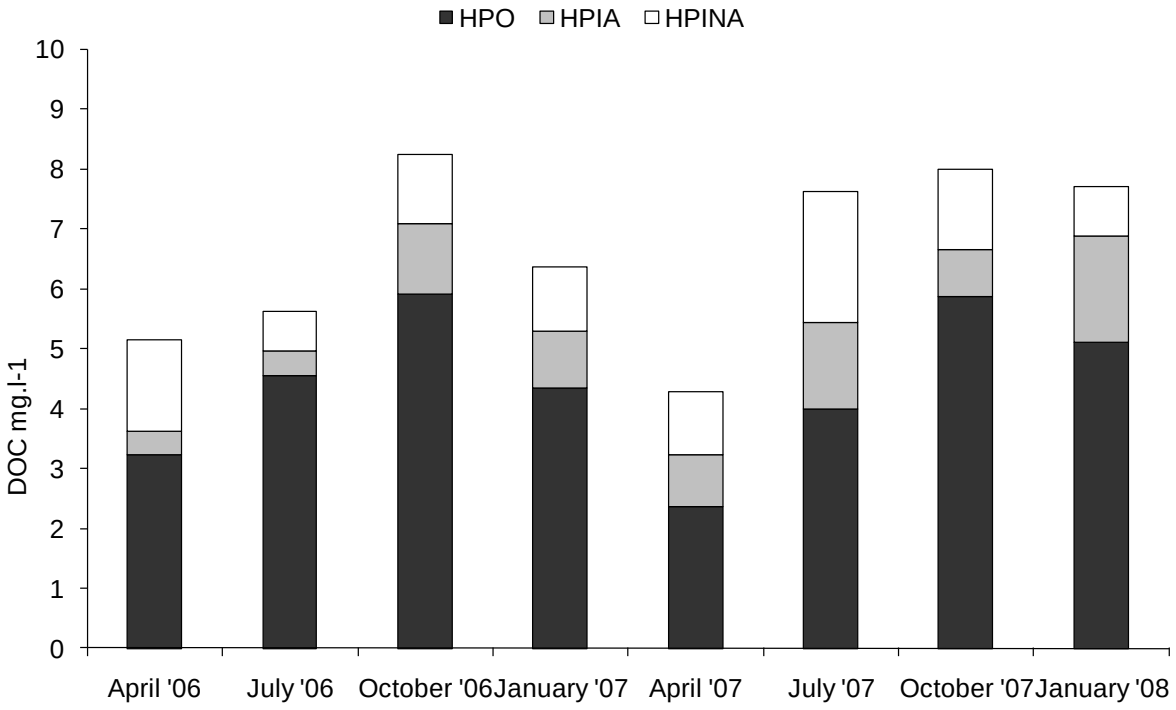


Figure 4.3 – Site 1 fractionation results

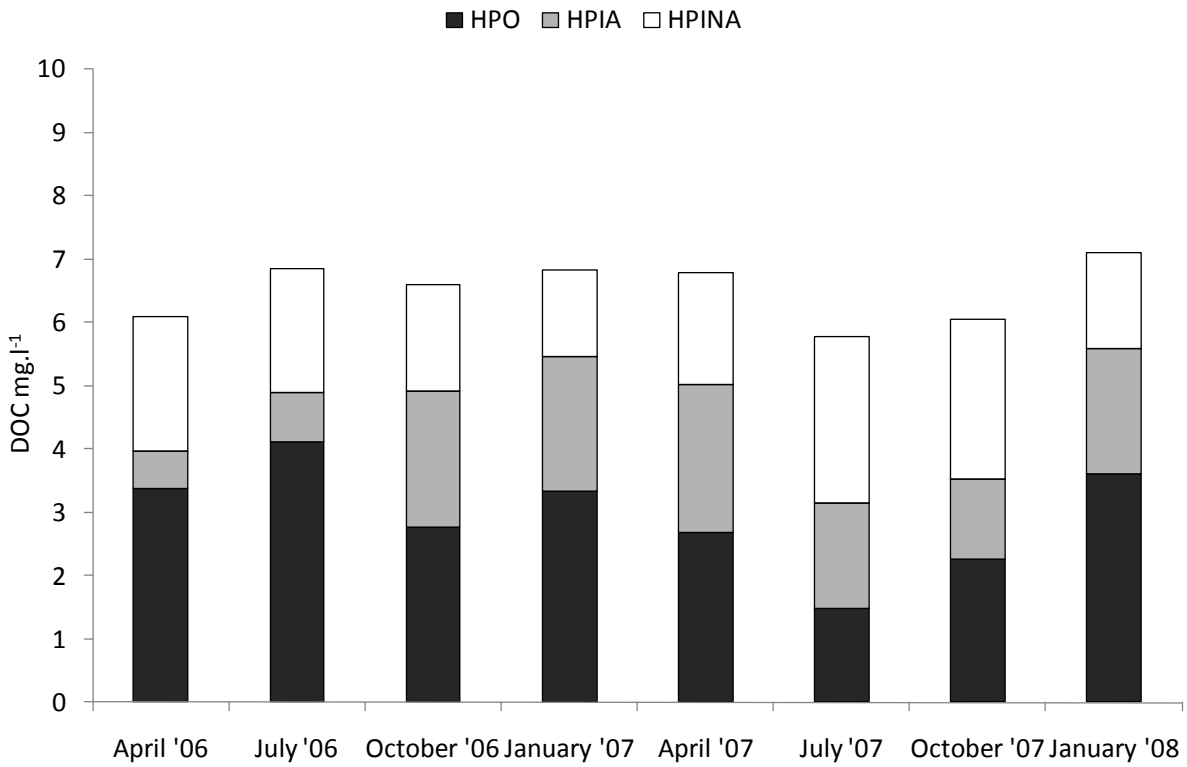


Figure 4.4 – Site 5 fractionation results

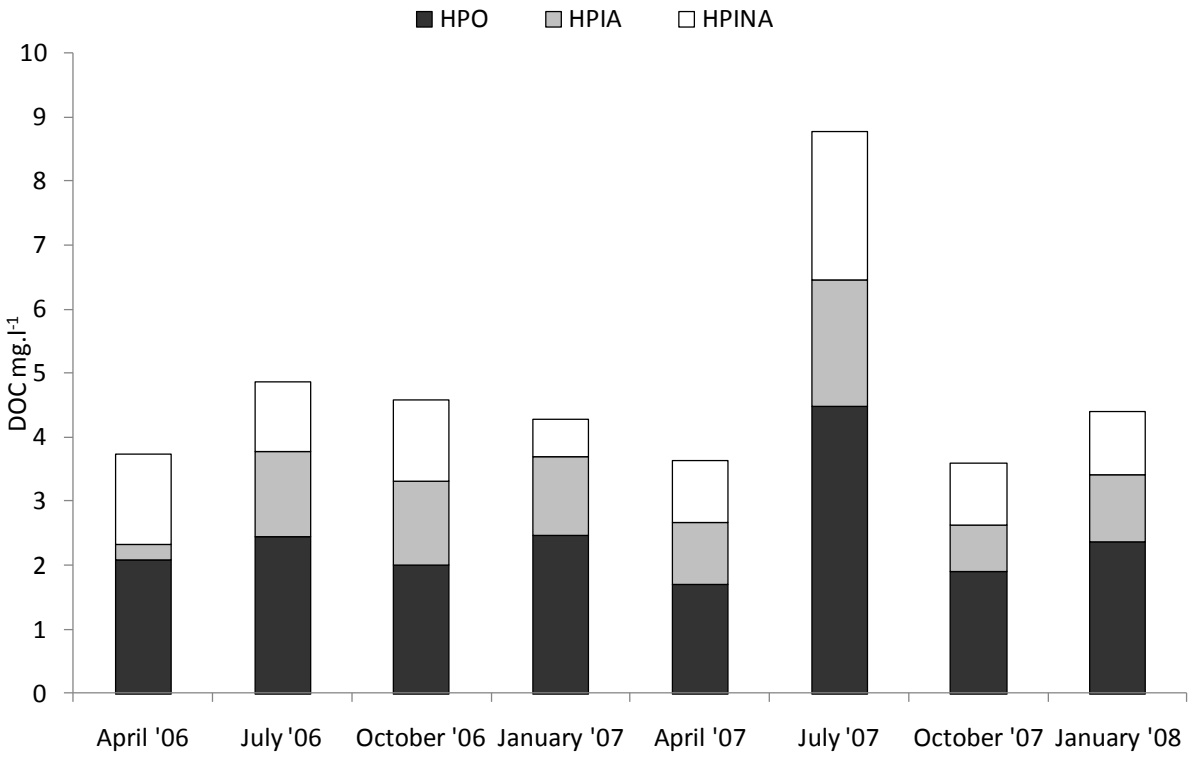


Figure 4.5 – Site 13 fractionation results

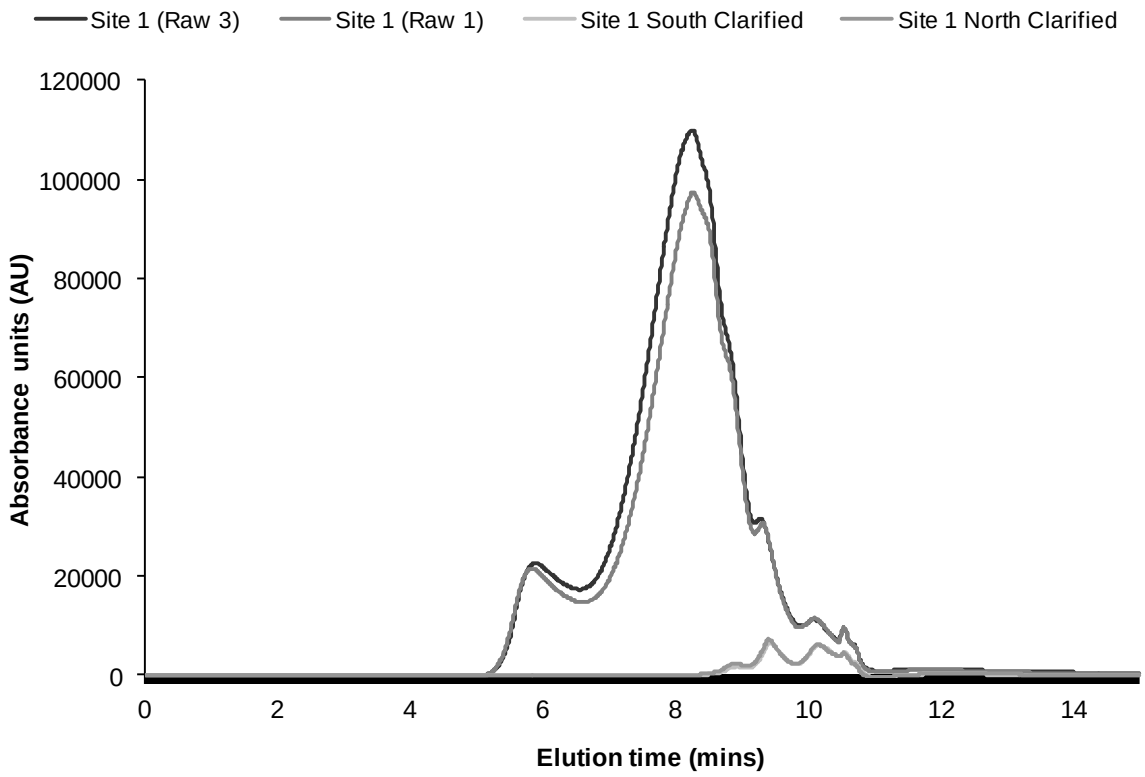


Figure 4.6 – Typical Site 1 WTW removal HPSEC

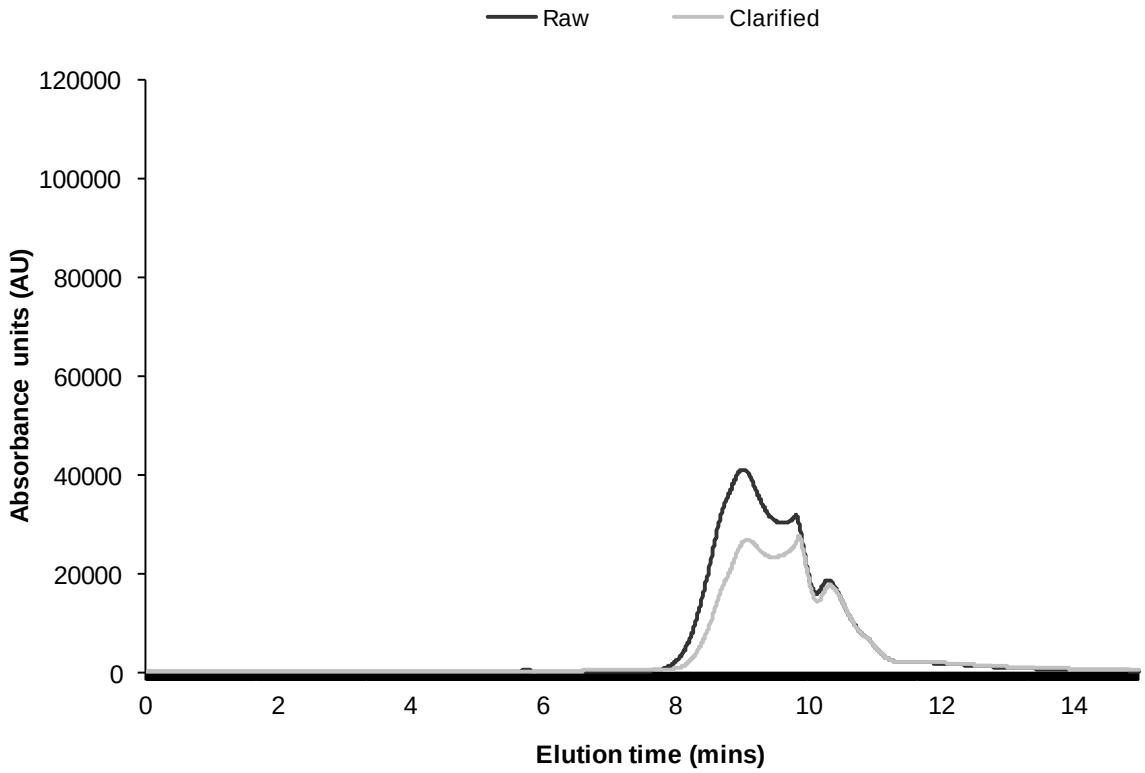


Figure 4.7 – Typical Site 5 WTW removal HPSEC

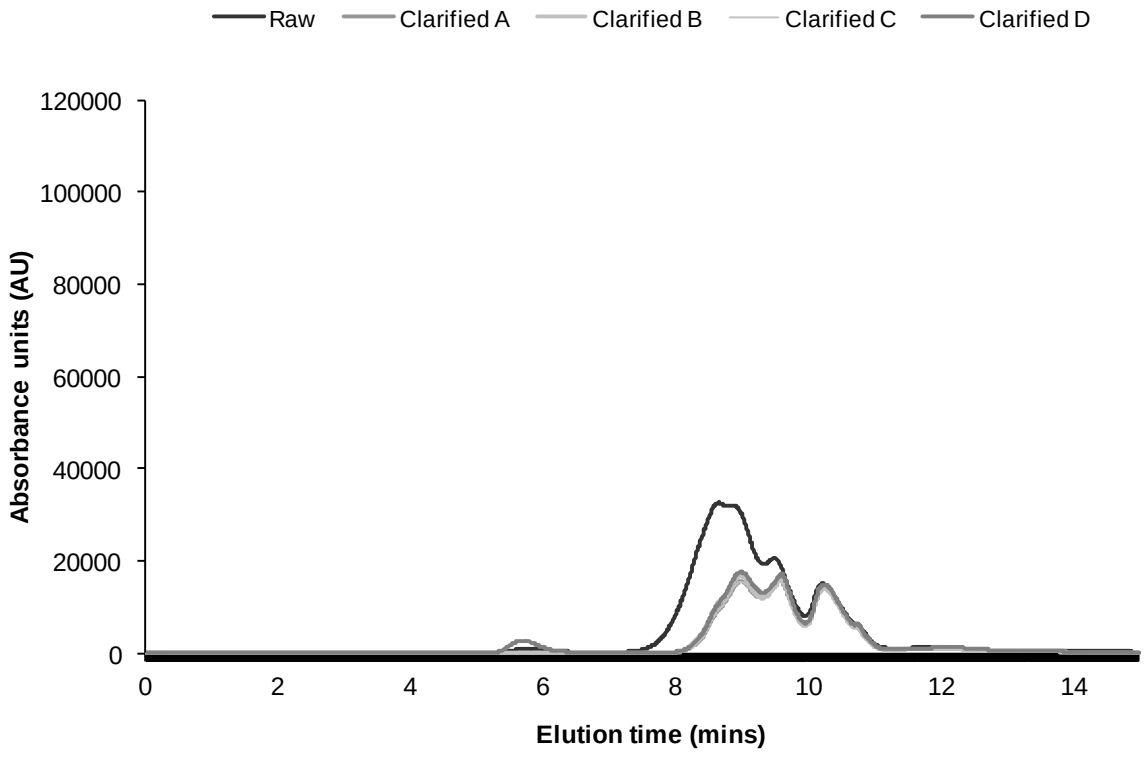


Figure 4.8 – Typical Site 13 WTW removal HPSEC

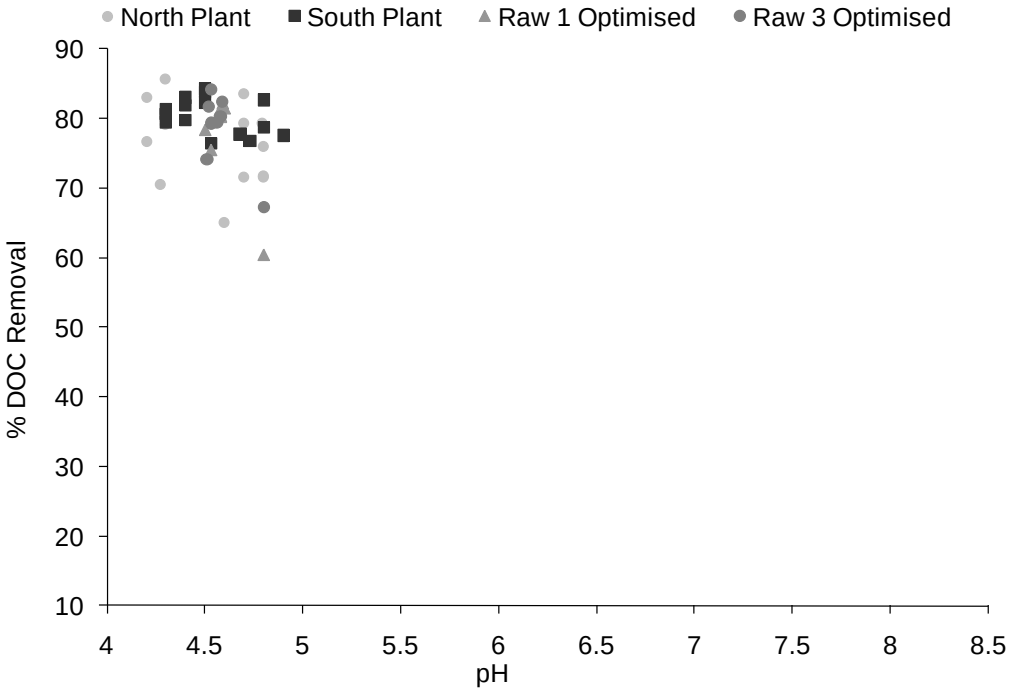


Figure 4.9 – Site 1 low pH and correct plant performance

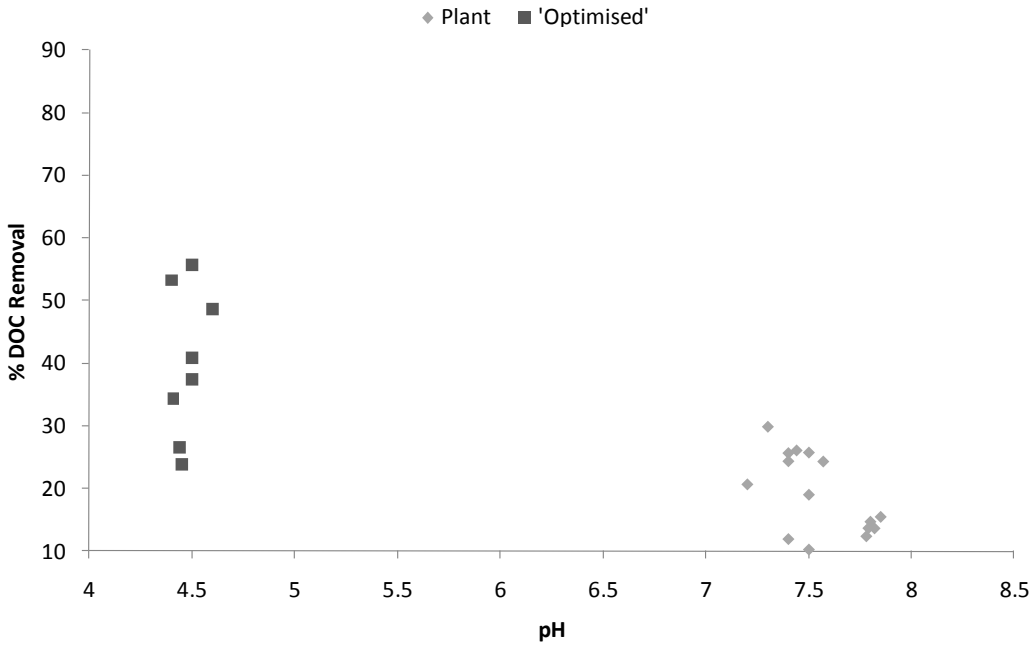


Figure 4.10 – Site 5 low pH and correct plant performance

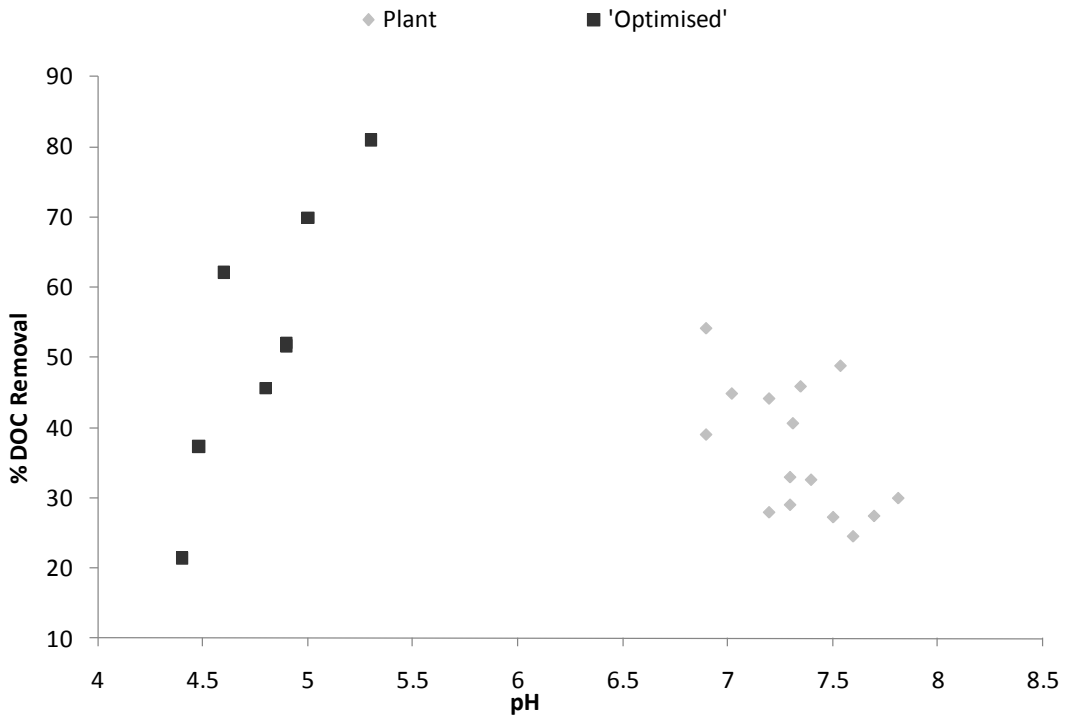


Figure 4.11 – Site 13 low pH and correct plant performance

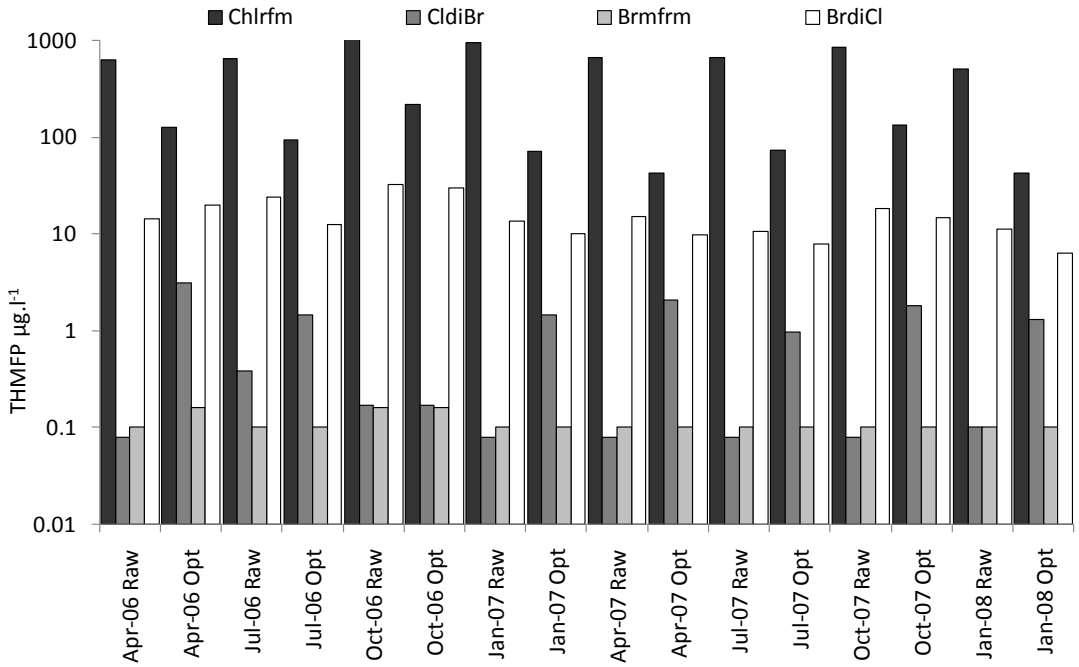


Figure 4.12 - Site 1 Raw 3 THMFP

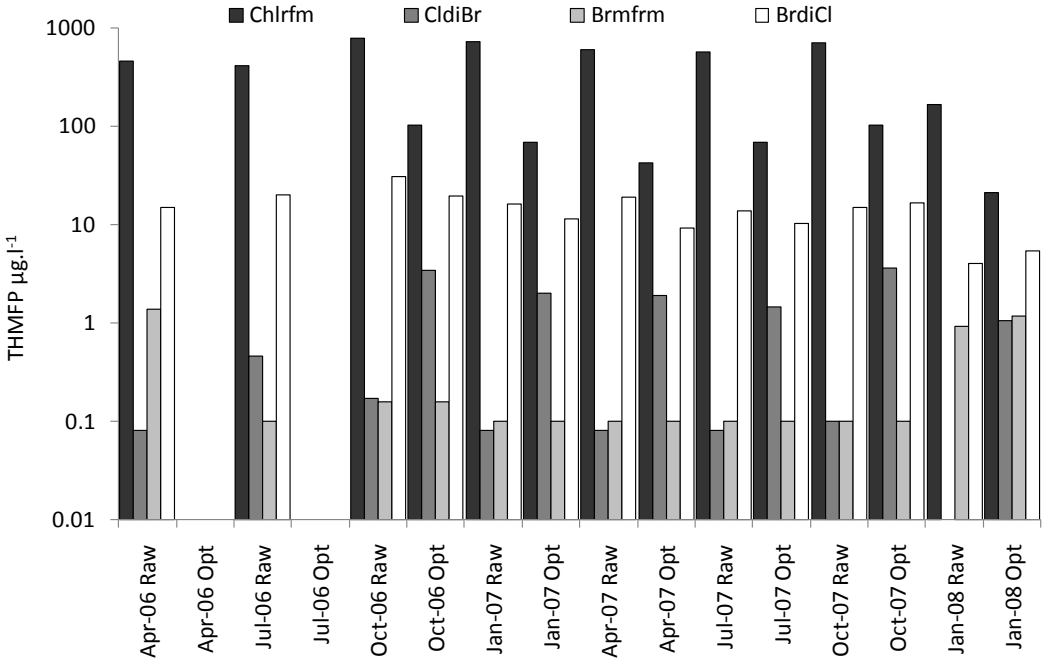


Figure 4.13 – Site 1 Raw 1 THMFP

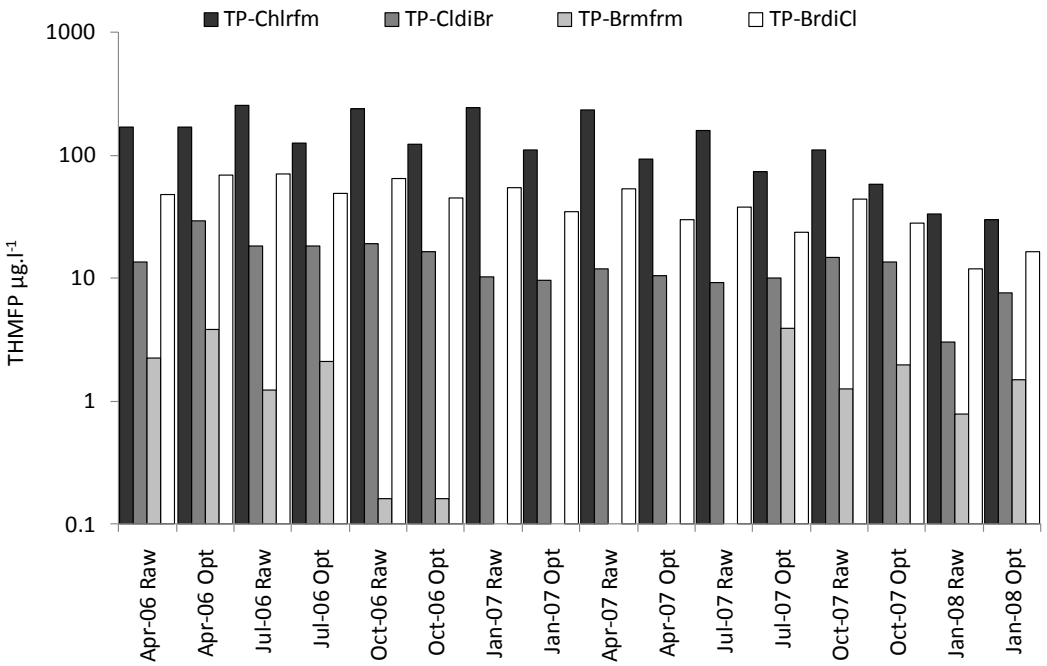


Figure 4.14 – Site 5 THMFP

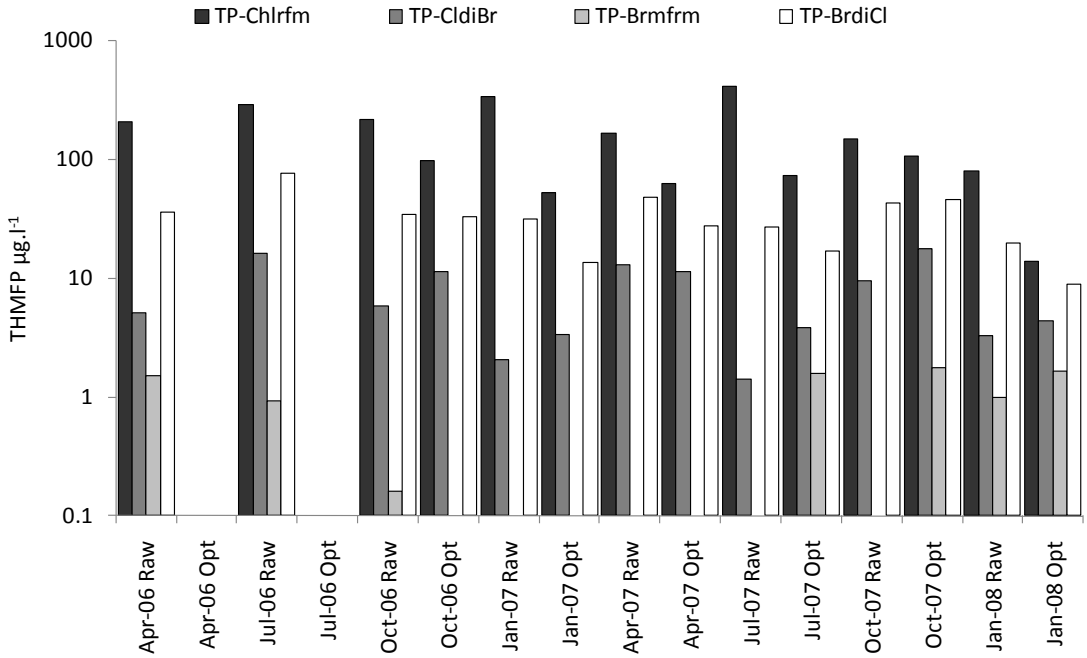


Figure 4.15 – Site 13 THMFP

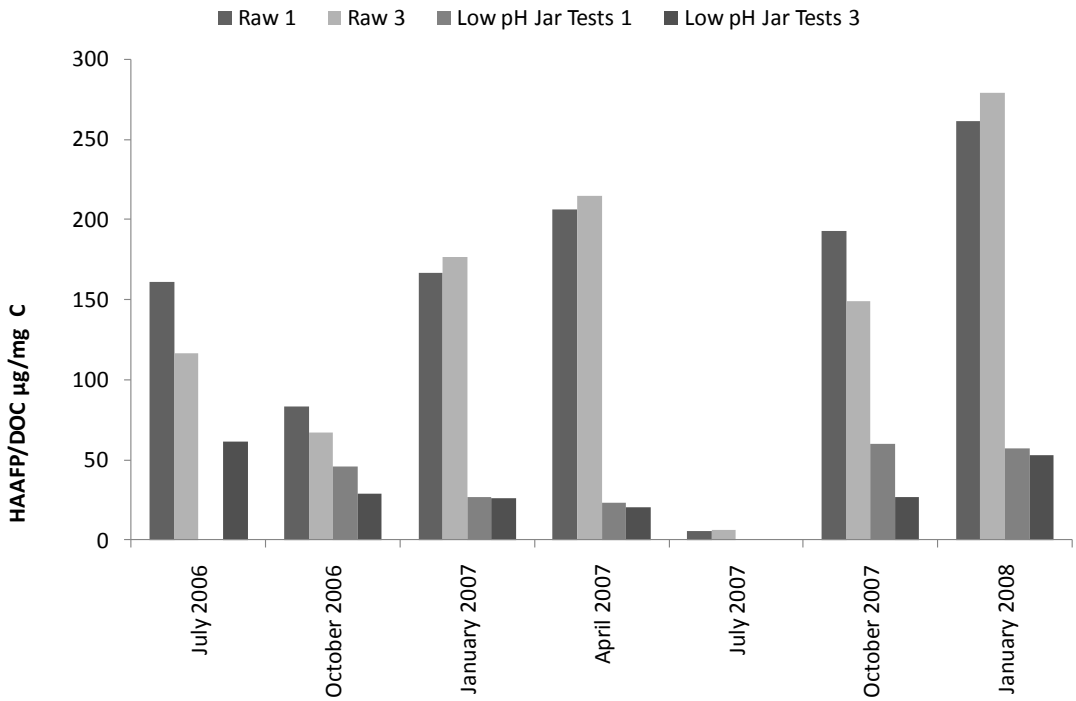


Figure 4.16 – Site 1 HAAFP

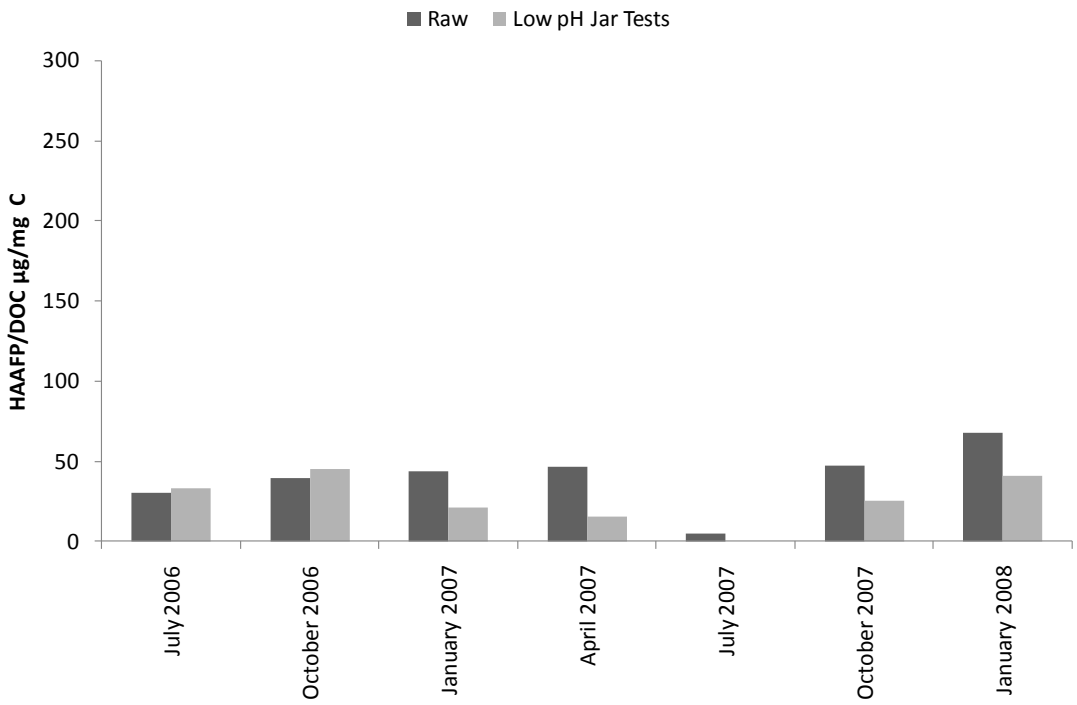


Figure 4.17 – Site 5 HAAFP

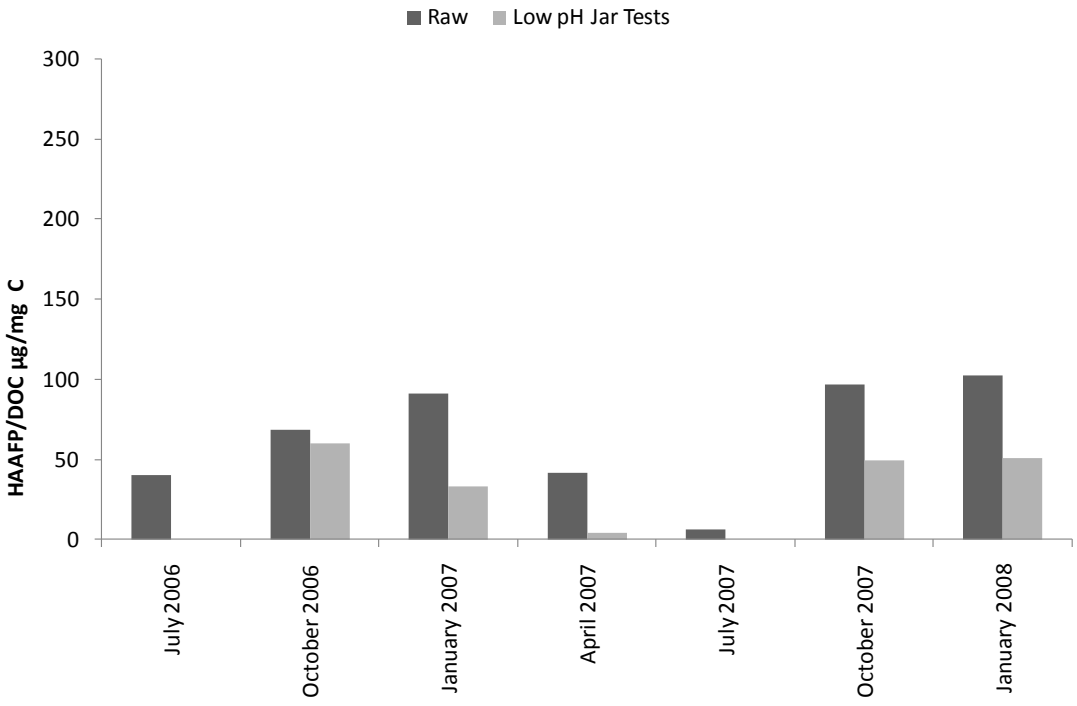


Figure 4.18 – Site 13 HAAFP

Chapter 4 Tables

Table 4.1 – Average Site conditions

Site	pH	UV_{254} ($abs.m^{-1}$)	Turbidity (NTU)	DOC ($mg.l^{-1}$)	DOC STDev	SUVA* ($L\ mg^{-1}\ m^{-1}$)	HPIA ($mg.l^{-1}$)	HPINA ($mg.l^{-1}$)	HPIA ($mg.l^{-1}$)
Site 1 (Raw 1)	6.3	29.4	1.5	5.5	1.3	5.1	0.9	1.2	1.0
Site 1 (Raw 3)	6.1	35.7	1.7	6.7	1.7	5.1	0.9	1.2	1.0
Site 2	7.9	12.9	7.6	5.3	1.3	2.3	1.4	1.8	1.4
Site 3	7.6	8.9	1.4	3.1	0.6	2.7	0.8	0.9	0.8
Site 4	7.6	19.4	4.0	7.1	1.3	2.6	2.2	2.0	2.2
Site 5	7.9	12.2	1.1	5.6	0.3	2.2	1.6	1.9	1.6
Site 6 (Raw Site 6)	6.7	11.0	1.1	2.7	0.6	3.9	0.4	0.7	0.4
Site 6 (Raw Bartley)	6.7	11.0	0.8	2.8	0.5	3.9	0.7	0.8	0.7
Site 7	7.5	8.9	3.9	2.9	0.9	2.8	0.7	1.1	0.7
Site 8 (Raw Staunton)	7.6	11.8	1.2	4.3	0.5	4.5	1.1	1.5	1.1
Site 8 (Raw Foremark)	7.8	11.4	1.2	4.0	0.4	2.8	1.0	1.1	1.0
Site 9	7.4	8.7	3.5	2.8	0.9	2.9	0.7	0.9	0.7
Site 10	7.4	13.2	7.2	4.4	1.2	2.9	0.9	1.3	0.9
Site 11	7.6	13.1	1.6	4.7	0.8	2.7	1.1	1.5	1.1
Site 12	7.2	13.2	5.7	4.0	1.3	3.1	1.1	0.9	1.1
Site 13	7.4	14.6	6.9	4.3	1.2	3.2	1.1	1.2	1.1
Site 14	6.8	24.3	3.5	6.7	0.9	3.5	1.6	1.5	1.7
Site 15	7.4	14.8	3.1	4.5	0.8	3.1	1.0	1.2	1.0
Site 16	7.6	14.7	3.7	5.7	1.1	2.5	1.4	1.6	1.4

***SUVA – Specific UV Absorbance**

Table 4.2 – Average plant coagulant pH and percentage DOC removal

Site	Average Coagulation pH	Average DOC Removal (%)
Site 1 Raw 1	4.6	76.8
Site 1 Raw 3	4.5	80.5
Site 5	7.6	18.5
Site 13	7.3	36.1

Chapter 5. Relating organic matter characterisation to DBP formation using data mining

5.1 Introduction

The analysis of larger data sets can become problematic due to it being a time-consuming process, but also the likelihood of missing key trends is increased. Statistical techniques are increasingly being used in data analysis as they allow the rapid analysis of large and multidimensional data sets. Principal component analysis (PCA) is a method that reduces data dimensionality by performing a covariance analysis between factors. Consequently, it is suitable for data sets in multiple dimensions. PCA is a method of reducing and simplifying data sets by means of linear transformations. PCA detects significant patterns in the data and has been used here as a means of identifying patterns in the data produced and expressing data in such a way as to highlight their similarities and differences. Discriminant analysis is a tool to determine an optimum combination of variables to provide the maximum discrimination between sites (Spencer et al., 2007). Data are split into functions, function one providing the most variation. Functions are orthogonal to one another and so their contributions to the discrimination do not overlap (Spencer et al., 2007).

The work presented in this chapter focuses on objective (i)

To evaluate the use of existing characterisation methods for the investigation of NOM composition and in the identification of key trends in NOM character, existing and achievable removal and DBP formation.

In order to ascertain the suitability of data mining techniques for NOM characterisation, data from the 24 month NOM characterisation study used in Chapter 4 was analysed using discriminant and PCA. Discriminant analysis and PCA were chosen as they have been successfully utilised in similar studies (Baker, 2002, Haag and Westrich, 2002, Spencer et al., 2007) and use of a widely available statistical software package (SPSS Inc. Version 16.0). Further statistical analysis to identify potential correlations with DBP formation potential were performed using stepwise regression analysis. In particular, the following questions were addressed;

- Can data mining techniques (Discriminant analysis and PCA) identify key trends in NOM character and distinguish between large numbers of NOM sources?
- Can PCA identify potentially overlooked relationships between NOM character and DBP formation potential?
- Can data mining techniques offer a significant advantage over existing data analysis tools?

In this chapter, sites are assigned numbers for the purpose of statistical investigation identification, these are shown in table 5.1.

5.2 Discriminant analysis

Discriminant analysis was performed using monthly NOM characterisation data and quarterly fractionation data. As previously mentioned, discrimination analysis highlights the factors which provide the greatest contrast between variables; which in this case were

source waters. Discriminant analysis identifies two functions, comprising of the variables, in this case NOM characterisation results, which vary the most between sites. It is then possible to use these results to identify patterns in raw source waters. Table 5.2 illustrates that the main component of discriminant function one is SUVA, a prime indicator of NOM character obtained by dividing the UV absorbance of a given sample at a wavelength of 254 nm, by the DOC concentration in $mg.L^{-1}$. The main component in discriminant function two is the total HPO fraction in $mg.L^{-1}$. These two functions are able to achieve a broad spread of the sites, implying these variables are important for site discrimination (figure 5.1). On the basis of the discriminant analysis, the sites can be split into three main types.

Type 1 consists of sites 1, 7 and 13, which are typically moorland source waters, characterised by higher total fractions of high molecular weight HPO material, NOM consisting of aquatic humic and fulvic acids. Type 1 waters usually react favourably to coagulation and flocculation processes, with large amounts of total DOC removed during treatment, but the large scatter visible in figure 5.1 demonstrates that this water type is the most susceptible to seasonal variation. Type 2 waters include sites 5, 6, 8, 9, 10, 12, 14, 15 and 16. Type 2 waters contain a mixture of molecular weights, and HPI and HPO NOM. Due to the HPI fraction in the water, sites are usually less amenable to standard treatment processes, but good removal can still be achieved with optimised processes. Type 2 waters are intermediate water types between types 1 and 3. Finally, Type 3 waters include sites 2, 3, 4 and 11. These sites exhibit high levels of HPI material in raw source waters and removal of total DOC is generally below 25%. Type 3 sites are typically situated in lowland, more urbanised catchments and are less influenced by seasonal variability.

5.3 Principal component analysis

5.3.1 Type 1 waters

For Type 1 waters the first three components of PCA are able to characterise up to 74% of raw water (table 5.3). Component 1 is characterised by high UV, NTU, DOC, peak T intensity and smaller organic material as seen in HPSEC peaks 3 and 4 (figure 5.2). Component 2 is characterised by high SUVA, peak C intensity and larger OM as shown by HPSEC peak 1. The first two components characterise up to 64% of Type 1 raw source waters. Samples identified by season show a clear distinction between periods (Figure 5.2), with some overlap between quarters. Winter months (1) have predominantly higher UV, NTU and DOC, with the majority of spring samples (2) having lower SUVA and high MW OM, demonstrated by HPSEC peak 1. Component 1 results demonstrate spring months have a reduced DOC content, peak T intensity, and composition of lower MW OM demonstrated by HPSEC peaks 3 and 4. This indicates that type 1 sites will most likely have lower amounts of HPI NOM in raw water during spring months. Summer (3) and autumn (4) raw waters show no distinct pattern with component 1 results, but component 2 suggests sites have continuously lower levels of high MW NOM (HPSEC peak 1), and lower SUVA. Further inspection of data confirms a decreased SUVA value within these periods, correlating with an increased percentage of HPI OM in source waters.

5.3.2 Type 2 waters

Type 2 waters typically consist of mixed molecular weight and HPI/HPO content. Totalling nine sites, Type 2 waters have been split according to catchments for greater identification of potential trends. There are two major catchments operating in this area, feeding the Severn and the Trent rivers.

5.3.2.1 Type 2 waters – Severn catchment

Component 1 for Type 2 Severn catchment waters (Figure 5.3) is high in UV, DOC, peak C intensity, and HPSEC peaks 1 and 3. Component 1 follows a similar trend to Type 1 component 1 results, with UV and DOC being dominant classification characteristics. Component 2 is high in peak T intensity and HPSEC peak 5, and is negatively correlated with peak C emission. The two components characterise 64% of Type 2 Severn catchment raw waters (table 5.4). Seasonally, there are clear distinctions between autumn and winter raw waters. Winter months have higher UV, DOC and peak 1 NOM. Waters exhibit a dominance of HPO OM, with low turbidity. Spring and summer samples have less HPO material (figure 5.3) demonstrated by lower peak C intensities and lower overall DOC. Autumn waters have a mixed proportion of HPO and HPI material, but typically have elevated NTU. Turbidity levels are expected to rise during the autumn months due to intense rainfall after a dry summer, bringing more NOM from the catchment into surface water.

5.3.2.2 Type 2 waters – Trent catchment

Component 1 for Type 2 Trent catchment raw waters characterises 43% of source water, and is high in UV, DOC, peak C intensity, peak 1 and SUVA (figure 5.4). Component 2

characterises an additional 22% with high NTU, totalling 65% of Type 2 Trent source waters (table 5.5). Figure 5.4 illustrates that the Trent catchment Type 2 sites exhibit less seasonal variation compared to other sites. Winter samples generally have lower turbidity levels, with the well-documented autumn flush demonstrated by a high turbidity. Spring samples exhibit lower levels of humic and fulvic acids, indicated by a negative component 1 placement.

5.3.3 Type 3 waters

The first two components for type 3 PCA shown in Figure 5.5 gave a combined total characterisation of 58% (table 5.6). Component 1 is high in UV, DOC, peak C intensity and HPSEC peaks 1, 3 and 5. PCA has shown for each water type that UV, DOC and peak C intensity are significant variables for raw water characterisation. Component 2 is high in peak C emission and HPSEC peak 4, with a negative correlation with HAAFP. Type 3 waters appear somewhat resistant to seasonal influences (figure 5.5). Spring and summer months generally fall below zero with component 1 and therefore are expected to have reduced UV, DOC and peak C intensity compared to winter and autumn months. Autumn and winter months provide no identifiable trends.

5.4 DBP formation and removal

Percentage average removals of THM according to type are displayed in table 5.7. Individual THM component removal is comparable to each individual THM before and after treatment. Removal of chloroform, TTHMFP and HAAFP precursors are greater at Type 1

sites and percentage removal declines at the more lowland, HPI dominated sites. This corresponds to studies by Kitis et al. (2002) and Croué et al., (1993) which demonstrate that the HPO fraction of DOM were the most reactive components and had the greater potential to form DBP. In addition, Type 2 Trent catchment sites have a higher incidence, and therefore increased removal of brominated THM such as chlorodibromide, bromoform and bromodichloride.

Stepwise regression is a statistical tool using regression modelling to define an optimal equation for predicting variables, and was used to define relationships between the independent variables in this investigation. Stepwise regression results for the combined groups between TTHM, TTHMFP and THAAFP are shown in table 5.8. The closer to 1.0, the greater the correlation between the two variables, and therefore the reproducibility of the equation and reliability of the variable to predict the selected DBP. The statistical significance levels for the sites are all 0.01, as the number of data points for Type 1, n=32, Type 2 Severn n=38, Type 2 Trent n=40 and Type 3 n=29. Stepwise regression results showed that on average yearly data for Type 1 raw waters shows positive relationships between HPSEC peaks 5, 4 and 3 with chlorodibromide and HPI material with bromodichloride and TTHMF. HPSEC peaks 4 and 5 are indicative of low MW, HPI OM. There is also a strong positive correlation between HAAFP and HPSEC peak 1, an increasingly dominant section of high MW NOM which is effectively removed through traditional metal salts coagulation in Type 1 sites.

Averaged Type 2 Severn catchment data shows strong correlations between THM bromoform and HPSEC peak 3, and bromodichloride with HPSEC peak 4 (table 5.8),

suggesting a link between smaller, low MW OM and brominated THM. These findings are similar to those published in 2007 by Hua et al., where greater amounts of brominated THMs were formed by HPI NOM (Hua and Reckhow, 2007). Contrasting to Type 1 waters, HPO has a strong regression relationship with TTHMFP in Type 2 Severn waters, providing a potential indicator for total THMFP. A regression relationship is evident between NTU and HAAFP, however at 0.68 R^2, the strength of the relationship has a strong potential for over/under-estimation. Type 2 Trent catchments have far fewer significant stepwise regression relationships with potentially formed DBP (table 5.8) compared to the Severn catchment Type 2 sites, with only a 0.60 R^2 correlation with UV and chloroform. Stepwise regression relationships provides little insight into a link between Type 3 sites and DBP formation, with only weak correlations produced between raw water type and HAAFP and percentage HPINA.

Site-specific stepwise regression relationships obtained on each of the four THM and the statistical significance of the R^2 relationship are shown in table 5.9. This table identifies the variables with which stepwise regression relationships occurred and the statistical significance. The statistical significance levels for the sites remain high for the number of data points, with site 1 as 0.01, n=14; 0.05 for site 4, n=8. Type 1 waters show only relationships occurring with chloroform, with HPO material being a common precursor. Where there is a dominance of HPI material in the raw waters, particularly HPINA, relationships with the remaining THM are also found.

5.5 Discussion

Results in this study found that discriminant analysis can distinguish between sites using NOM characteristics. Discriminant analysis identified SUVA and HPO content as the two factors which allowed the greatest distinctions between sites in the Severn Trent region, two factors that could easily have been identified without using a statistical package. The advantages of discriminant analysis lie that with a large number of sites, it is a more reliable tool that for categorising sites and identifying the parameters that are most important.

Using discriminant analysis it was possible to split Severn Trent Water source waters into three distinct types based on the raw water. It did not however provide any additional insight into understanding the water character, just a means of identifying defining characteristics. This output was very valuable when used with PCA however.

PCA on these three identified types of waters allowed data to be filtered to its statistically significant variables. PCA identified that Type 1 waters showed distinct seasonal variations, with late summer and autumn periods experiencing notably higher total DOC concentrations and HPO content, which is in concurrence with NOM characterisation literature (Goslan, et al., 2002, Tipping et al., 1999). For Type 2 waters, PCA identified that they contained a mixture of both HPO and HPI material and that seasonal trends were not observed and that Type 3 waters seasonal trends were in the autumn and winter months. PCA does not identify new characteristics for NOM, it instead identifies which characteristics are dominant at each site, and in turn allows you to characterise the quality of the waters, and essentially predict treatment issues or trends.

The purpose of stepwise regression analysis was to identify precursors for DBP formation but to also identify links with NOM characterisation method so that a particular method could be used on site to predict DBP levels. Stepwise regression analysis was employed to identify trends between NOM character and DBP formation. It successfully confirmed that chloroform was the dominant DBP on HPO dominant sites (Croué et al., 1993, Goslan et al., 2009), however it was also able to identify trends between NOM fractions and specific DBP. This could potentially be used to identify which sites were susceptible to producing particular DBP, and treatment conditions could reflect that.

Interestingly, the results also showed that HPO organic material didn't correlate with THMFP, THM and HAAFP at all sites, the only other correlation is with TTHMFP at Type 2 Severn waters, indicating chlorine demand could be greater from HPI material. Where there is a dominance of HPI material in the raw waters, particularly HPINA, relationships with the remaining THM were also found. Concentrations of chlorodibromide, bromoform and bromodichloride at HPI dominated sites indicate the removal of HPI material is more integral to reducing DBP formation levels. It also suggests that research published by Bond et al., in 2009 stating that the formation of DBP was not related to NOM character, more to the formation of other DBP is correct for brominated DBP formation, that formation of the three previously mentioned DBP were linked. The research did conclude that many DBP trends were site specific and not linked to seasonal trends. This therefore leads to the assumption that NOM character is not the definitive factor for DBP formation.

5.6 Conclusions

Data mining techniques were used to identify key trends in NOM character and were able to distinguish between large numbers of NOM sources. They provided a method of statistically characterising NOM into 'types' and identifying the parameters that could characterise water quality the most accurately – and identify relationships between sites and characterisation parameters that may have been previously overlooked.

Discriminant analysis and PCA would not be able to identify relationships with DBP formation as the two currently appear only distantly linked currently, which is due to the type of data provided by NOM characterisation tools.

Stepwise regression analysis was able to rapidly assess large datasets for relationships with DBP and NOM characteristics, and is a tool that is frequently used in statistical analysis. Discriminant analysis and PCA would best be employed to identify key parameters for analysis prior to this.

Discriminant analysis and PCA are still valuable research tools, but the outcomes of the investigation need to be identified thoroughly first in order to achieve the full potential of these particular analysis tools.

Chapter 5 Figures

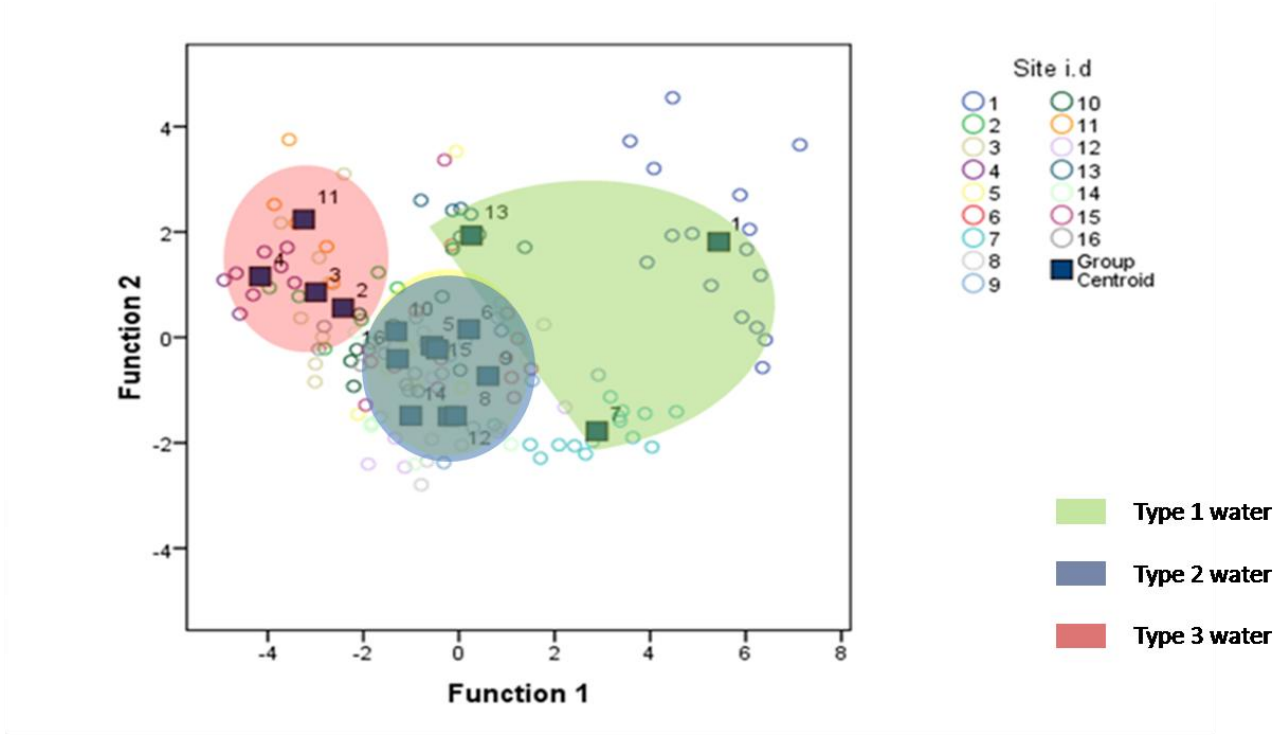


Figure 5.1 – Discriminant analysis for all sites

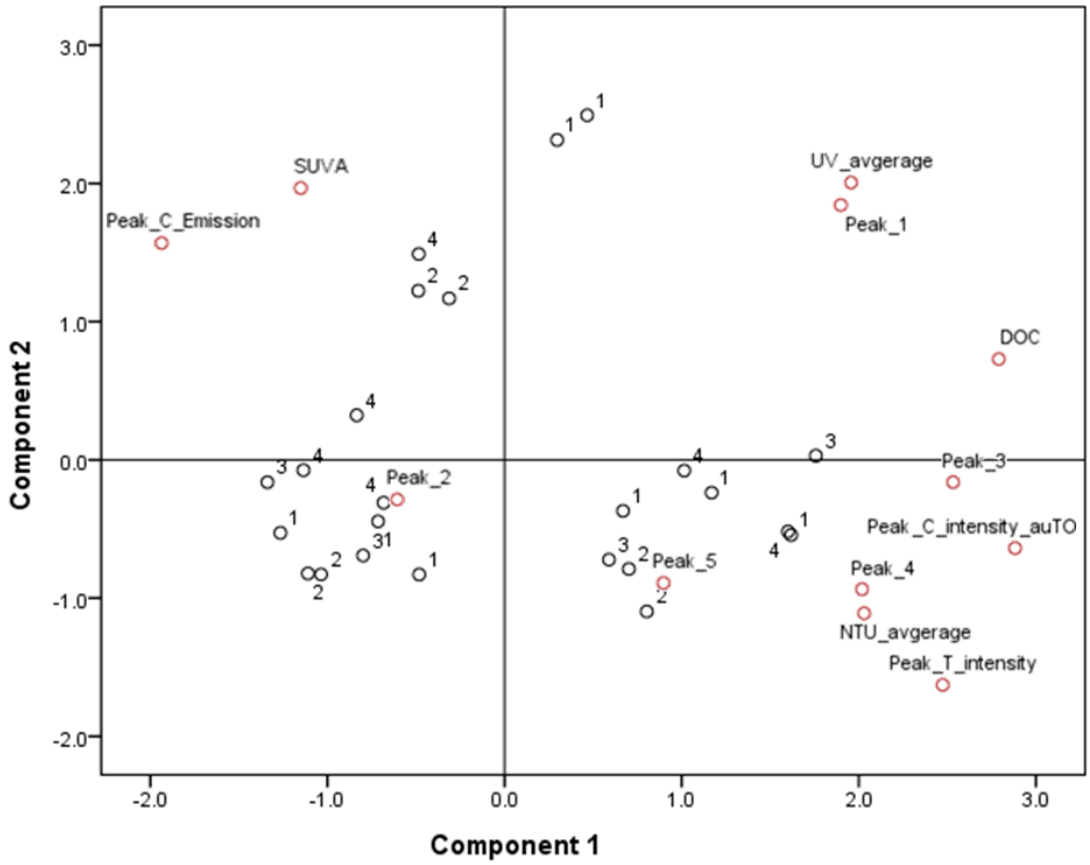


Figure 5.2 - PCA component plot

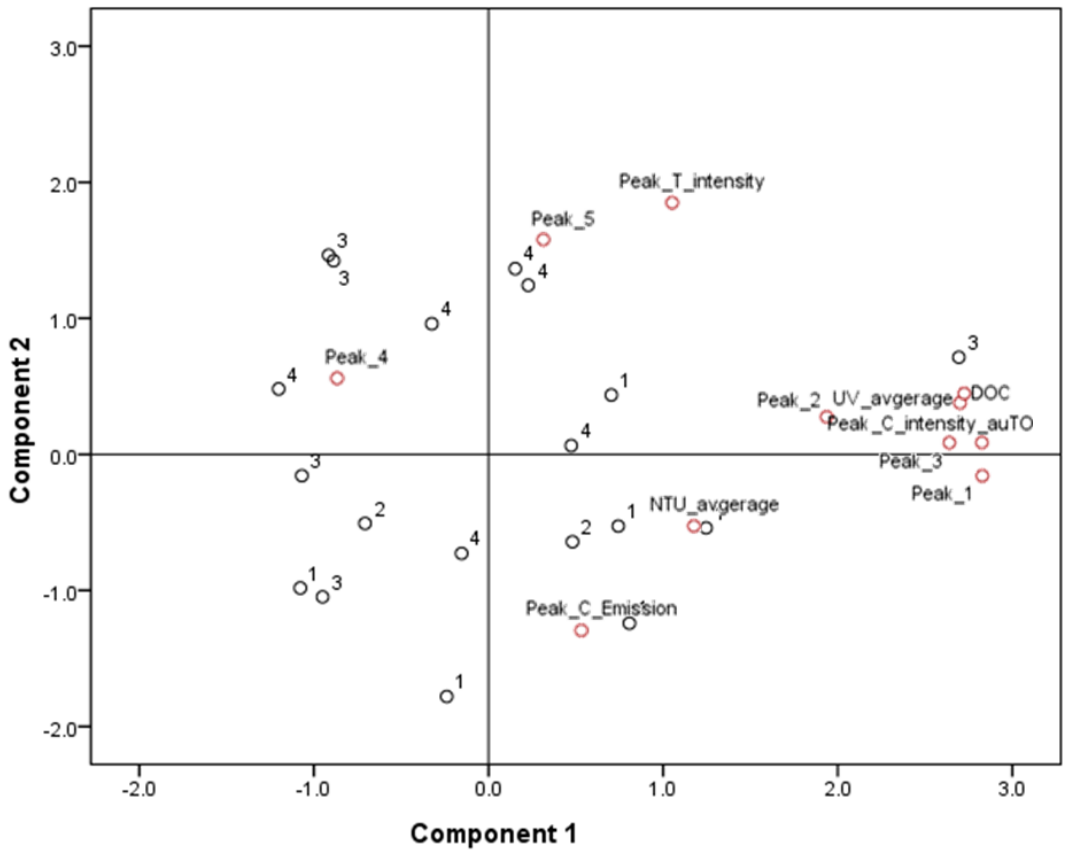


Figure 5.3 – PCA component plot for Type 2, Severn catchment raw water

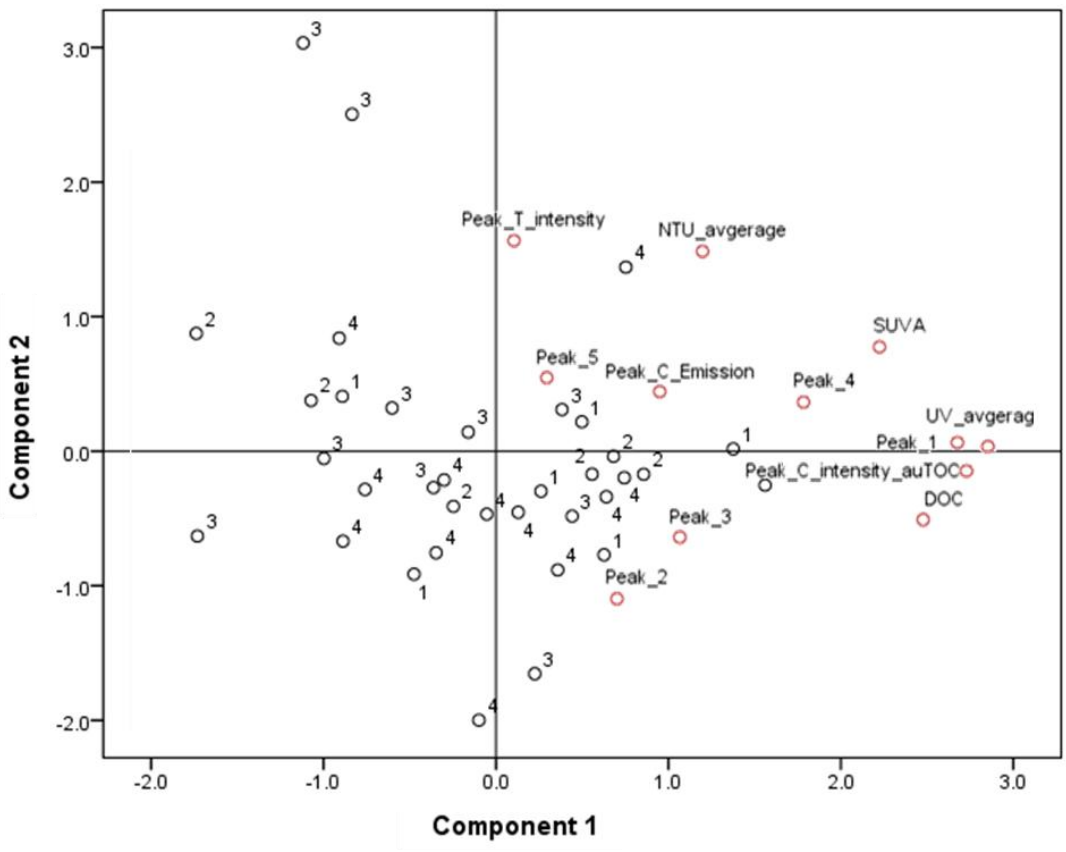


Figure 5.4 - PCA component plot for Type 2, Trent catchment water

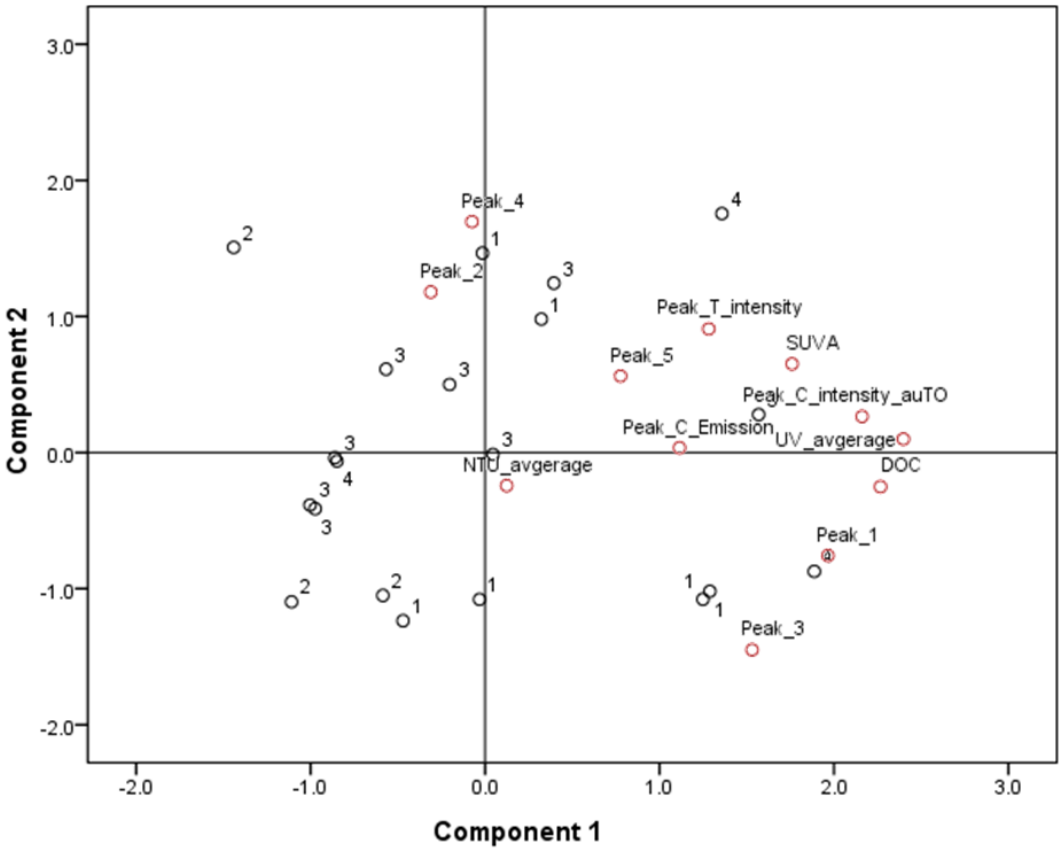


Figure 5.5– PCA component plot for Type 3 raw water

Chapter 5 Tables

Table 5.1 – Site reference numbers

Site	
1	Site 1
2	Site 16
3	Site 2
4	Site 5
5	Site 10
6	Site 15
7	Site 6
8	Site 9
9	Site 12
10	Site 11
11	Site 4
12	Site 7
13	Site 14
14	Site 3
15	Site 13
16	Site 8

Table 5.2 – Discriminant analysis function structure matrix

	Function	
	1	**2**
$SUVA_{254}$	0.76*	0.34
HPO	0.11	0.84*
HPIA	-0.16	0.46
HPINA	-0.17	0.41

* Largest absolute correlation between each variable and any Discriminant function.

Table 5.3 – Principal component analysis for Type 1 waters

Total Variance Explained[a]

	Initial Eigenvalues			Extraction Sums of Squared Loadings		
Component	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.52	46.02	46.02	5.52	46.02	46.02
2	2.19	18.28	64.30	2.19	18.28	64.30
3	1.22	10.12	74.42	1.22	10.12	74.42
4	0.99	8.25	82.67			
5	0.69	5.81	88.47			
6	0.64	5.32	93.79			
7	0.34	2.86	96.65			
8	0.17	1.41	98.06			
9	0.15	1.26	99.31			
10	0.06	0.52	99.84			
11	0.02	0.15	99.98			
12	0.01	0.02	100.00			

Extraction Method: Principal Component Analysis.

a. Only cases for which Raw/Clarified = 0 are used in the analysis phase.

Table 5.4 – Type 2 Severn catchment PCA

Total Variance Explained[a]

	Initial Eigenvalues			Extraction Sums of Squared Loadings		
Component	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.13	46.63	46.63	5.13	46.63	46.63
2	1.91	17.37	63.99	1.91	17.37	63.99
3	1.22	11.12	75.12	1.22	11.12	75.12
4	0.98	8.94	84.05			
5	0.72	6.55	90.60			
6	0.55	5.02	95.62			
7	0.29	2.62	98.23			
8	0.10	0.86	99.10			
9	0.06	0.57	99.67			
10	0.02	0.21	99.87			
11	0.01	0.13	100.00			

Extraction Method: Principal Component Analysis.

a. Only cases for which Raw/Clarified = 0 are used in the analysis phase.

Table 5.5 – Type 2 Trent Catchment PCA

Total Variance Explained[a]

	Initial Eigenvalues			Extraction Sums of Squared Loadings		
Component	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	6.43	42.83	42.83	6.43	42.83	42.83
2	3.27	21.83	64.66	3.27	21.83	64.66
3	2.49	16.61	81.27	2.49	16.61	81.26
4	1.34	8.90	90.17	1.34	8.90	90.17
5	0.76	5.06	95.23			
6	0.43	2.86	98.08			
7	0.29	1.92	100.00			

Extraction Method: Principal Component Analysis.

a. Only cases for which Raw/Clarified = 0 are used in the analysis phase.

Table 5.6 – Type 3 PCA

Total Variance Explained[a]

	Initial Eigenvalues			Extraction Sums of Squared Loadings		
Component	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.77	39.78	39.78	4.77	39.78	39.78
2	2.22	18.49	58.27	2.22	18.49	58.27
3	1.96	16.34	74.60	1.96	16.34	74.60
4	0.87	7.29	81.89			
5	0.69	5.72	87.61			
6	0.55	4.55	92.15			
7	0.31	2.60	94.75			
8	0.23	1.90	96.64			
9	0.22	1.81	98.45			
10	0.13	1.06	99.51			
11	0.06	0.48	99.99			
12	0.00	0.01	100.00			

Extraction Method: Principal Component Analysis.

a. Only cases for which Raw/Clarified = 0 are used in the analysis phase.

Table 5.7 – Average percentage removal of DBP

Raw water Type	Chloroform % removal	Chlorodibromide % removal	Bromoform % removal	Bromodichloride % removal	TTHMFP % removal	HAAFP % removal
1	47	0	0	20	47	49
2 – Severn	46	1	4	25	43	46
2 - Trent	46	11	11	28	41	42
3	43	1	0	20	31	41

Table 5.8 – Stepwise regression relationship in average raw water quality for combined groups, calculated over the period March 2006 – February 2008. R^2 regression relationships shown in brackets, statistically significant relationships (95 percentile) in bold.

Type	Chloroform	Chlorodibromide	Bromoform	Bromodichloride	TTHMFP	HAAFP
1		Peak 5 ***(0.78)*** Peak 5 + Peak 4 *(0.97)* Peak 3 ***(0.58)*** Peak 3 + % Removal ***(0.85)***		HPINA *(0.82)*	HPI *(0.50)*	Peak 1 ***(0.90)***
2 (Severn)			Peak 3 *(0.97)*	Peak 4 *(0.98)*	HPO *(0.99)*	NTU ***(0.68)***
2 (Trent)	UV_{254} ***(0.60)***	UV_{254} ***(0.31)***		Peak T intensity ***(0.26)***	HPI *(0.58)*	Peak 4 *(0.50)* Peak T intensity *(0.23)*
3	Peak T intensity ***(0.40)***			UV_{254} ***(0.36)***		% HPINA *(0.50)*

Table 5.9 - Stepwise regression relationship in raw waters for individual sites. R^2 regression relationships shown in brackets, statistically significant relationships (95 percentile) in bold.

	Site	Chloroform	Chlorodibromide	Bromoform	Bromodichloride
Type 1	**1**	HPO *(0.64)* HPO + HPIA *(0.77)*			
	7	HPO *(0.65)*			
	13				
Type 2	**5**				
	8	DOC *(0.93)*	HPO *(0.76)*	HPINA *(0.68)*	
	9				
	10			HPINA *(0.51)* HPINA + NTU *(0.85)*	
	14				
	16				
	15		NTU *(0.62)*		
Type 3	**3**		HPO *(0.81)*	HPINA *(0.84)*	
	2		UV_{254} *(0.63)* UV_{254} + NTU *(0.85)*	HPIA *(0.78)*	UV_{254} *(0.52)*

Chapter 6. DBP precursor removal through low pH coagulation

6.1 Introduction

Recent research has concentrated on alternative treatment for the removal of NOM in drinking water. Investigations have considered the use of ultrafiltration membranes, anionic exchange resins, activated carbon and heated aluminium oxide particles (HAOP). Ultrafiltration membranes and HAOP are examples of processes which are typically ineffective against the HPI fraction, but effective at removal of humic acids (Cai et al., 2008, Lowe and Hossain, 2008). These treatment alternatives can however be costly, and investigations of current plant performance at Severn Trent sites in chapters 4 and 5 indicate that plants are not operating at optimal conditions for NOM removal.

Literature suggests that improved DOC removal can be achieved using enhanced or optimized coagulation techniques (Cromphout et al., 2008, Edzwald and Tobiason, 1999, Matilainen et al., 2010). Such techniques involve either increasing the coagulant dose (enhanced) or optimizing coagulation dose and pH.

The work in this chapter focuses on objective (iii):

To establish whether current treatment conditions are capable of removing increased amounts of NOM in order to reduce DBP formation.

In order to evaluate the suitability of optimised coagulation for increased NOM removal, a low pH coagulation strategy was conducted. Site 13 WTW was chosen because of its highly

variable raw water quality (due to direct river abstraction) and is heavily influenced by small changes in weather conditions. Consequently, optimised treatment conditions at Site 13 are difficult to predict and rarely achieved. Flow data and raw WTW TOC data from Site 13 is shown in figure 6.1.

The low pH coagulation strategy was devised so as to cover a wide range of pH and dose scenarios in order to provide a comprehensive outlook on potential THM formation. The performance of five different coagulant doses (2, 4, 6, 8, 10 $mg.l^{-1}$) was assessed at five pH values (4.0, 4.5, 5.0, 5.5, 6.0), making a total of 25 jar tests per sampling period (table 6.1). Results were used to identify the best treatment strategy for NOM removal and DBP minimisation. The economical impact of each strategy was also considered. In particular, the following questions were addressed;

- Can DOC removal at Site 13 WTW be improved with low pH coagulation?
- Do seasonal changes in NOM have an overtly detrimental effect on DOC removal at Site 13 WTW?
- Can DBP formation potential be reduced by low pH coagulation at Site 13 WTW?
- What are the practical issues of a low pH coagulation strategy?

6.2 Results and Discussion

6.2.1 DOC, UV_{254} and turbidity removal

Over the three sampling periods turbidity levels altered most noticeably with a sharp increase in September and November months, as show in table 6.2. This could be attributed

to the summer flush period, with heavier rainfall leaching larger amounts of organic material from the surrounding catchment. July raw waters have the highest concentrations of DOC of all three sampling periods, but experience a greater affinity to low pH coagulation with increases shown throughout the pH ranges.

An additional three jar tests were performed in September due to the difficulty in DOC removal at higher pHs. September water was unresponsive at lower coagulant doses, so an additional dose (12 $mg.l^{-1}$) at pH 5, 5.5 and 6 was assessed. This substantiates operators' claims for increased coagulant dose after the summer flush period as the NOM composition is predominantly HPI material, making typical NOM removal processes less effective at a higher pH, which is discussed further in Section 6.3.

DOC removal for the July jar tests shows a non-linear removal of DOC with pH, with a lower rate at higher pH levels. Figure 6.2a illustrates that DOC removal is greatest at pH 4 to 4.5 but a plateau of removal at these pH levels is also reached, indicating they are more amenable to lower coagulant doses, reducing treatment costs without affecting removal quality. The increased removal by the reduction in pH also indicates that the coagulation mechanism occurring is charge neutralisation instead of sweep flocculation, and that sites could improve NOM removal by altering the coagulation mechanism. To achieve similar removal at higher pH levels larger coagulant doses are needed, increasing treatment costs.

September percentage DOC reductions, shown in figure 6.2b, display an incremental change in DOC removal with increased coagulant dose. September DOC removal was the lowest on average during all three sampling periods. This could be attributed to the large amount of

HPI material in the raw water (Section 6.3). Lower pH jar tests were again more amenable to DOC removal at lower coagulant doses, with the highest removal achieved at pH 5 with a dose of 10 mg.l^{-1}. pH 5.5 and 6 exhibited only 56% and 55% DOC removal respectively even at an elevated dose of 12 mg.l^{-1}. The limited capacity for removal at the higher coagulant dose ranges indicates that overdosing leads to charge reversal rather than neutralisation, so although improvements are seen, there is a maximum volume coagulation process can achieve in terms of NOM removal. There was an increase in DOC reduction at the larger doses at the high pH, indicating DOC removal at operation pH is coagulant dose dependant. September is an ideal month for low pH coagulation. Percentage DOC removal is worse at the higher pH, however the pH would need to be lowered to below 5 so its cost benefits would have to be considered to determine feasibility.

DOC removal for November shown in figure 6.2c demonstrates a rapid initial decrease of DOC with the addition of coagulant. Coagulation is more effective at lower doses with pH levels 4-5, but all pH ranges suffer overdosing at the largest coagulant dose of 10 mg.l^{-1}. A maximum removal of 72% is achieved for November raw waters, and most surprisingly, these peaks in removal occur in the higher pH range, which could be attributed to November waters being more responsive at higher coagulant doses even at high pH. SC04 (pH 5, dose 8 mg.l^{-1}) and SD05 (pH 5.5, dose 10 mg.l^{-1}) have the highest removal rates of the jar test period, DOC removal values of 70 and 71% are achieved at a pH of 4.5. November waters have a dominance of HPO material which could be attributed to increased removal. Higher pH levels are able to remove a large percentage of OM, but these are also achievable at lower pHs with a cost saving in coagulant.

6.2.2 Fractionation

Fractionation profiles offer an indication of potential DOC removal. It is widely noted that coagulant demand is controlled by the HPO content of raw waters, with maximum achievable removals reached more consistently when there is a dominant HPO fraction in raw waters (Jarvis et al., 2005c, Jung et al., 2005, O'Melia et al., 1999). Figure 6.3 compares the raw water fractions from each sampling period. As mentioned previously, July waters were more responsive to low pH coagulation, with significantly higher DOC removal rates achieved, potentially indicative of a dominant HPO content. September waters are predominantly HPI, negatively impacting raw water treatability.

November NOM characteristics return to proportions similar to July levels, indicating an end to the summer flush period. November water was also highly coloured, had the highest turbidity levels and proved more responsive to coagulation than September raw waters.

6.2.3 HPSEC

July HPSEC plots shown in figure 6.4 indicate the fraction most successfully removed were the larger fraction absorbed first onto the column. As no direct relationship to particle size is abailable, this fraction is likely to consist of HPO material. Lower pH jar tests still proved relatively ineffective in removing the smaller, hydrophilic fractions, but overall a large percentage of total DOC was effectively removed, meaning a removal of potential THM and HAA precursors. At a dose of 10 $mg.l^{-1}$ there is little variation in the type or qualtity of material removed between the various coagulation pHs, however similar levels of removal

are experienced at lower pHs without the high coagulant dose. Regardless of dose or pH, the HPO fraction in the July waters is so high it will be removed through conventional coagulation and flocculation. The removal of the smaller faction, thought to be HPI material, can be seen to be challenging at all pH and coagulant dose combinations, with none exceeding 50% removal of that particular fraction.

HPSEC profiles for September waters in figure 6.5 show lower pH coagulation jar tests have the maximum removal of all molecular size fractions, with the removal of the smaller molecules consistently less than 50% for all jar tests. The jar tests performed at a higher dose of 12 $mg.l^{-1}$ show little difference between all three pH ranges but removal of the various molecular size ranges are similar to those using a smaller coagulant dose at lower pHs. The majority of removal occurring is of the larger molecular size fractions shown by a shift in the profile start to a retention time of eight minutes. A larger volume of material is removed with an increase in coagulant dose even at lower pHs, however the HPSEC profiles are further verification of the advantages of low pH jar tests for this season and the character of raw water experienced.

HPSEC profiles for November shown in figure 6.6 demonstrate how the differences in removal of all size fractions at the various pHs decrease with the a higher coagulant dose. At a dose of 10 $mg.l^{-1}$ there is very little difference between the types of molecular removal and quantity at all pHs. pH 6 jar tests consistently leave a shoulder of material eluted onto the column at approximately 8.2 minutes. This material is more successfully removed with a reduction of 0.5 pH, indicating higher pHs are not removing material which even a small change in pH is able to. Considering the type of material removed by coagulation, Site 13

water typically removes the larger molecular fraction more easily, a trend which has become apparent throughout all seasons, with the smaller HPI fractions still resisting removal efforts.

Table 6.3 shows the removal of each size fraction in July. Peak area was estimated by approximating Gaussian curves underneath the peaks using Origin 8.0 Software. Analysis of peak location was undertaken to establish peak location (according to retention time), the Origin software then calcualated the area underneath the peaks. Peak areas were then tabluated and underwernt statistical analysis. Similar methods have been employed for HPSEC peak analysis by Chow et al., (2008), where HPSEC measurements were analysed to determine MW removal during alum jar tests (Chow et al., 2008c). From table 6.3, peak I is identified as the most easily removable fraction, with good removals of peak V also experienced. Peaks I and V are expected to correspond with the most HPO, and the most HPI material in a sample respectively. Peaks II – IV are less effectively removed, however there is a notable difference in removal between the different pH and coagulant dose ranges and in some cases (peak II), analysis showed approximately 20% more prganic material could be removed.

Percentage peak removal for September HPSEC results in table 6.4 follows the same trend, as does November percentage removals in table 6.5. As the peak identification is unable to directly correspond to specific molecular weights, it is difficult to identify which particular size fraction is affected however, it is clear that smaller molecular weight NOM are not being effectively removed by conventional coagulation and flocculation processes, however increased removal is possible with lower pH coagulation. This is largely dependent on

source water characteristics however, as September and November waters had increased amounts of HPI organics, which would negatively impact on removal rates.

6.2.4 Zeta Potential

Coagulation of NOM is dependent on the charge neutralisation of the outer surface charge of particles. With a minimisation of electrostatic repulsion between particles, maximum achievable removals can be reached. Zeta potential is a measure of particle surface charge, so is used as an indication of coagulation efficiency. Previous studies have shown zeta measurements above +3 mV are an indicator of overdosing at the works (Sharp et al., 2006c).

In July jar tests (figure 6.7a); zeta potential measurements taken at the start of the slow mix stage indicated optimal zeta levels were not being reached until the increased coagulant dose was administered. Zeta potential results in figure 6.7a show a sharp decline in DOC, NTU and UV levels as the lower limit of the recognised optimal range (-10 mV to + 3 mV) is approached. UV levels are the most responsive to the addition of coagulant. Turbidity values reached a plateau much sooner, at lower coagulant doses, suggesting that the 'optimal range' for turbidity removal could even be extended to -15 mV. This indicates turbidity removal would be consistent at any coagulant dose/pH combination. Even though overall DOC removal is better within the 'optimal' zeta potential range, significant and uncorrelated variations are evident.

Data reproduced in table 6.6 indicates pH is the more dominant factor in July waters, and a small reduction in pH would lead to greater benefits in water quality and operational costs. Table 6.6 also shows water quality values DOC, NTU and UV_{254} increased at 10 mgL^{-1} when coagulation pH was reduced to 4. This suggests that when coagulating at lower pHs, a high coagulant dose leads to an overdose of coagulant, resulting in a complete charge reversal and restabilisation of the colloid complex and consequentially poor NOM removal.

As previously stated, an additional three jar tests were carried out on September samples as zeta potential measurements suggested that at pH 6 the optimal zeta potential range was not reached so an increased coagulant dose of 12 $mg.l^{-1}$ was applied (table 6.7). Figure 6.7b shows that even when results just broach the -10 mV optimal zeta potential range cut-off DOC values are still highly variable whereas NTU and UV_{254} values settle into a linear pattern more effectively, the cause of which could again be due to the character of the raw water as determined by fractionation profiles shown in Section 6.3.2. Waters with a largely HPI content are prone to decreased removal rates as HPI is less amenable to removal by conventional coagulation. The discrepancies with charge density seen between the three sampling periods are also attributable to the greater quantity of HPI NOM in the sample. Work by Sharp et al., (2004) describes how charge density from HAF and FAF matter is nearly two orders of magnitude greater than HPI material. This potentially raises concerns when using zeta potential as an indicator for DOC removal as charge density data is driven by the HPO NOM, which is more readily removed.

With November waters, optimal zeta potential is more difficult to achieve with higher pH levels and at pH 6 the optimal range is only reached with a coagulant dose of 10 $mg.l^{-1}$. This

could be attributed to a much higher initial turbidity levels than other sampling runs. Lower pH levels are more responsive to DOC, turbidity and UV_{254} removal but November waters were also less responsive to pH alterations, as shown in table 6.8.

All three sampling periods do show a positive relationship between zeta potential and removal of UV_{254}, turbidity and DOC, however variations between the sampling periods highlight potential limitations of using zeta potential as an indicator of coagulant performance. In all three sampling periods, and particularly in September and November when overall DOC was more difficult to remove, there is still significant variation with DOC removal within the 'optimal zone' of -10 to +3 mV. This is also noted by Sharp et al., (2004) where it is highlighted that the optimal range for turbidity removal is broad, but for DOC is narrow. This could be attributed to the greater fraction of charged humic and fulvic material in the raw water dominating the surface charge, and the mechanisms of removal; the humic acid fraction is removed through a combination of charge neutralisation, complexation/precipitation and ligand exchange adsorption (Huang and Shiu, 1996), whilst fulvic acids are thought to be principally removed through adsorption pathways (McKnight et al., 1992).

The ratio of residual UV_{254} to residual DOC was greater in September and November, indicating the residual DOC is composed largely of lesser charged HPI NOM, which is not absorbing UV light and therefore not accounted for in the UV_{254} scans.

Zeta potential as an indicator of coagulant performance would therefore be best served at sites where HPO material is the dominant fraction. The -10 to +3 mV range for optimal

removal identified in zeta potential literature does provide an indicator of where increased removal of DOC would be achieved, but the success of which would be dependent on the HPI fraction of raw water and seasonal variations.

6.2.5 TTHM

DBP formation was measured in terms of THAAFP, TTHM and TTHMFP. TTHM were formed and fixed on site, whereas formation potential measurements for THM and HAA were undertaken in the laboratory.

TTHM for July were unusually low, a trend carried through the entire month's samples and would be expected to be higher considering the high HPO content of the raw water. Therefore July results are not included in this investigation as they are deemed unrepresentative.

September TTHM, as shown in figure 6.8a, show a decrease in THM formed with reduced pH and increased coagulant dose, corresponding to the removal of DOC – shown in figure 6.2b, Section 6.3.1. Lower pH levels still achieve the smallest TTHM formation and even with an increase in coagulant dose at pHs 5 to 6, TTHM are 50% more than at a pH 4 and 4.5. TTHM reported on site for the same time period were 23.10 μgL^{-1} so even at higher pH levels and a dose of 8mgL^{-1}, TTHM levels will be improved upon but there is still potential to reduce TTHM formation again at a lower pH.

When viewed alongside figure 6.2b, TTHM production for November (figure 6.8b) indicates a reduction with the additional removal of DOC, suggesting the occurrence of HPO material in raw waters is a dominant force in TTHM formation. TTHM production is elevated at higher pH levels although this does decrease with increased coagulant dose. Zeta potential measurements shown in section 6.3.4 indicate there was no overdosing throughout the jar tests which could demonstrate why on previous sampling periods there is an increase in TTHM formation at the higher coagulant dose ranges but not in the November sampling periods. Jar tests at pH 5 experience unusually low TTHM production levels at the 2 – 4 $mg.l^{-1}$ dose range, which is not supported by any of the removal or HPSEC data. Site 13 has an average annual TTHM value of 26.5 $\mu g.l^{-1}$, so whilst the experimental TTHM data is lower, they are comparable to the annual average at this site.

6.2.6 TTHMFP

TTHMFP concentrations show a similar relationship to TTHM as they do not increase with coagulant dose. TTHMFP are also indicative of DOC removal as figures 6.2a and 6.2b in Section 6.3.1 follow a similar pattern.

In July, figure 6.9a shows minimum TTHMFP levels at pHs below 5, however all pH levels yield THM concentrations below 100 $\mu g.l^{-1}$ at a dose of 10 $mg.l^{-1}$. Low pH jar tests are more effectively influenced by coagulant addition, with a staged decrease with addition more noticeable at higher pH levels. At pHs 4 and 4.5, TTHMFP levels remain reasonably static after a sharp initial decrease with increasing coagulant dose.

September samples in figure 6.9b have the highest THMFP levels, which could be reflective of the higher HPI content, particularly the HPINA content. Additional jar tests were required for the September sampling run as the water was less responsive to coagulant. September TTHMFP in figure 6.9b also follows a similar pattern to DOC removal. TTHMFP shows a more gradual reduction with increased dose, however lower pHs remain lower at forming THMFP, a trend continued within THAAFP results.

TTHMFP results for November jar tests in figure 6.9c also present a link to DOC removal dependency with formation potential. If TTHMFP concentrations are considered with HPSEC results, the initial reduction in formation potential could be linked to the removal of the first HPSEC peak, thought to be attributed to large molecular weight mater, particularly HPO. At higher dose ranges of 8 - 10 $mg.l^{-1}$ there is a greater contrast between TTHMFP through the coagulant dose range. This trend is not as extreme with formation potential levels at the lower pH ranges. A higher TTHMFP production at increasing pH ranges could indicate a potential trend occurring at site conditions with their coagulant pH of 7-7.5.

6.2.7 THAAFP

Similar to TTHMFP, July THAAFP levels responded to coagulation and flocculation treatment more effectively at a lower pH and lower coagulant doses (figure 6.10a). Jar tests at higher pHs were still successful in producing lower levels of HAAFP, however, this was achieved at the expense of a higher coagulant dose. The potential to overdose at pHs below 5, discussed previously, is pronounced with pH 4 and 4.5 at dose 10 $mg.l^{-1}$. An increase in THAAFP at

dose 10 mg.l^{-1} suggests that whilst organics removal is a strong influence on decreased HAAFP, overdosing of coagulant could also negatively impact on HAA formation.

September THAAFP concentrations in figure 6.10b also follow a similar pattern to DOC removal. TTHMFP gradually reduces with increased coagulant dose, however levels of TTHMFP formed by coagulating at a lower pH are continually significantly lower through all coagulant dose ranges, a trend continued within THAAFP results. This implies removal of TTHMFP and THAAFP precursors is greater by reducing coagulation pH. Overall, THAAFP values increased slightly throughout the sampling periods, however a marked trend is not apparent, indicating that raw water composition has little impact on HAA formation. This observation is confirmed with the statistical investigations in Chapter 5. Over a large dataset, only one stastically significant relationship was observed with THAAFP in surface waters (tables 5.8 and 5.9). In research literature, correlations are predominantly investigated between THAA and TTTHM. Only very few studies have successfully correlated THAA with TTHM, (Chang et al., 2001b, Hua and Reckhow, 2007, Krasner et al., 2006).

UK studies on TTHM and THAA formation also have contradictory results. Malliarou et al., (2006) found limited correlations between the two DBP but only with a small sample size. Also, work by the DWI on HAA formation found a correlation of 0.88 between TTHM and THAA on a study of three differing source waters (DWI et al., 2009). However, other UK studies by Bond et al., (2009), Bougeard et al., (2008) and Goslan et al., (2009) found unrelated formation of THAA and TTHM, and that THAA formation was dependant on the amino acid content of raw waters. Current published literature unfortunately concentrates on THM and emerging DBP, and even though HAA are included in such studies, many

investigations predominantly centre on the formation of such DBP with regards to coagulant type and not the rapid identification of precursors.

November THAAFP results show there is only a small variation between formation levels over the entire pH range (figure 6.10c). THAAFP is again significantly responsive to a reduction in THAAFP with increasing coagulant dose, even at higher pH levels, demonstrating that if a large and rapid reduction of levels were needed, a lower coagulation pH would be ideal. The only occurrence of an increase in THAAFP at a higher coagulant dose is with pH 6, which could be a trend carrying on at higher pH levels, influencing THAAFP levels occurring on WTW.

6.2.8 General DBP trends

Figure 6.11a illustrates the relationship between DOC and DBP formation potential. R^2 values for all the sampling periods can be seen in table 6.9. TTHMFP and THAAFP exhibit a higher correlation with DOC levels than UV and NTU, consistent with a reduction in the HPO fraction shown by HPSEC results. Actual TTHM formed and fixed immediately after jar tests show no relationship with DOC, or with any other water quality indicator recorded during the jar tests. These findings are in conjunction with THM and DOC investigations on the same source waters (Brown, 2009). It is possible that the most volatile THM precursors are the smaller organic materials but these reactions are masked by the long reaction times associated with formation potetial analyses. September results, shown in figure 6.11b, follow a similar pattern to July results, also experiencing high correlation between TTHMFP and THAAFP and DOC. Previous research on linking NOM character to DBP surrogates has

identified a link between the HPI fraction of NOM and HAA formation, especially for waters with a low humic content (Hua and Reckhow, 2007). This could attribute for higher levels of HAAFP in September waters, however fractionation profiles for the raw waters did not show a high HPI content in July raw waters. Research by Bond et al., (2009) states that formed DBP may also be surrogates, increasing DBP formation further, however in July, the temperature would also account for a greater DBP yield as it has a significant impact on formation (Bougeard et al., 2008).

Correlation between November THAAFP, TTHMFP and TTHM shown in figure 6.11c again show a definite relationship between DOC removal, (r^2 = 0.89 for TTHMFP, r^2 0.86 for THAAFP), and a weaker relationship between TTHM (r^2 = 0.60). There is correlation for TTHM, however there is a large amount of scatter occuring at the lower DOC levels indicating that this relationship may not be reliable with a larger dataset to be used as an algorithm for THM production on water treatment works. Unfortunately, sample sizes were not large enough for statistical significance, so correlations could alter for larger data sets.

As previously mentioned, formation potential resutls refer to a worst-case scenario as samples are left for 7 days. THMFP values are used to give the 'worst-case' scenario and are commonly linked to the humic acid content of source waters. THM, not THMFP are regulated however, so the value of THMFP in operations and monitoring on WTW are limited. THMFP does provide an insight to NOM character and composition and although they provide an unrealistic view of THM leaving the WTW, it can provide an indication of potential THM levels after a set time period when it is not practical to monitor THM in distribution.

6.2.9 Fluorescence

Fluorescence analysis were only performed on November samples as it was a late addition to the characterisation analyses, so a complete set of results showing seasonal profiles are unavailable. Clarified Peak C and peak T intensities can been viewed in table 6.10. Peak C intensity indicating fulvic like material is reduced with the increased dose of coagulant at all pH ranges (figure 6.12a). Peak C intensity is consistently higher at pH 6 demonstrating the poorer organics removal at this pH level compared to lower pHs. At higher doses of 8 and 10 mg L^{-1} there is little difference in peak C intensity at pHs 4 to 5.5, and all have a reduction of at least 66% peak C intensity after flocculation. Peak T intensity, indicating the presence of amino acid-like material is much more varied over the coagulant dose ranges. All pHs exhibit a decrease in Peak T with increased coagulant dose, but there is no clear trend occurring with pH ranges (figure 6.12b). It is believed that Peak T intensity may represent material which is more difficult to remove even in low pH coagulation and could be dependent on factors other than pH and dose.

Fluorescence results such as peak C intensity can be used as a rapid indicator of predicted removal on site (Bieroza et al., 2009b). Correlations with TTHMFP and individual THM shown in table 6.11 can also be used for quick on-site testing to assess coagulation and flocculation conditions. Therefore, the fluorescence data were investigated for correlations between water quality indicators and DBP. Peak C intensity correlates with the most number of individual factors, with stronger correlation. Peak C intensity could therefore be used to estimate total TTHMFP on site and be linked individually to bromodichloride.

Unfortunately here no strong correlations between Peak C intensity and THM, and the correlation with chlorodibromide is unlikely to be robust enough to accurately predict formation, however TTHMFP could provide an indicator of THM at customer tap and correlations shouldn't be discounted. Peak T intensity had fewer correlations but could also be used to estimate quantities of individual THMFP such as chlorodibromide.

6.3 Low pH coagulation costs & sludge production

Coagulation costs for the three sampling periods were obtained by calculating values for coagulant dose, HCl required to decrease pH, and sodium hydroxide (caustic soda) to increase pH post flocculation. Energy costs were not included as these were deemed to be common for all scenarios. The final values were calculated using the following formulae;

Coagulation costs:

Cost (£ tonne/d) = (dose (l/hr) * works production per day (Ml)/1000) * cost per tonne

Coagulant dose:

Dose (l/hr) = (1000/60/60 * (Ferric dose (mgL^{-1} Fe) *flow (l/s))) / (atomic weight/molecular weight * weight of coagulant)

Caustic Soda and HCL

Cost (£ per day per tonne) = dose (mgL^{-1}) *flow (Ml) *100 / chemical concentration (as delivered)/1000 * Acid cost (tonne)

All low pH coagulation results are higher than typical coagulation costs on site currently due to the added expense of lowering and reinstating the pH. Tables 6.12a – 6.12d outline individual low coagulation costs for each sampling period and Site 13 actual coagulation operating costs. Overall costs for November are the lowest due to a lower initial pH of 6.5 so doses of HCl and caustic soda can be reduced, however operational costs on site at this time were the highest due to an alum coagulant dose of 5.5 $mg.l^{-1}$, the highest of all three sampling periods. In all three sampling periods, low pH jar tests removed a maximum additional 1 mgL^{-1} off DOC plant removal rates at that time. This would not only reduce the amount of potential DBP formation by a minimum of 14mgL^{-1} at the highest pH of 6 with the same works dose, it would also increase filter run-times and aid processes further downstream.

Costs associated with DBP are displayed in figures 6.13a to 6.13c. As predicted, the cost of effective removal of potential DBP is entirely dependent on the raw water characteristics as well as the amount of chemicals needed for coagulation processes. July waters cost substantially less to treat as the raw water was more amenable to coagulation processes due to the dominance of HPO material in the sample. Following sampling periods had predominantly poorer removal, attributed to the sharp increase in turbidity and a larger dominance of HPI material in raw water fractions.

Sludge production was calculated using the Water Research council method (WRc, 1989) which provides an estimation of the amount of sludge produced based on raw water quality and chemical usage during treatment (he reasoning behind the choice to use this model is explored further in the discussions for this chapter):

Sludge solids (mg/L treated water)	= 2 x turbidity removed (NTU)
	+ 0.2 x colour removed (° Hazen)
	+ 2.9 x aluminium precipitated (mg Al/L)
	+ 1.9 x iron precipitated (mg Fe/L)

As aluminium coagulants were not used during this experiment the sludge calculated is estimated using raw water characteristics and Fe precipitation measurements. Hazen values were not recorded during the investigation, and so colour removed was estimated using an average colour measurement from a five year dataset. Sludge production rates can be seen in table 6.13, with Tonnes per day measurements calculated using works production rates for each sampling date. Sludge production compared to percentage DOC reduction is shown in figure 6.14. November waters had the greater sludge production due to previously discussed raw water character. As colour removal is an estimate, error bars based on colour extremes experienced within the five year data history are included in order to account for this.

As previously mentioned in Section 6.1, initial observations and seasonality, raw water quality in July is significantly more responsive to coagulation, compared with September and November samples. Due the lesser amount of NTU in the raw waters, total sludge production is considerably reduced compared with latter months. One of the largest problems at Site 13 is the variability of raw water characteristics, a common problem with direct river abstraction. September and November samples were more coloured with

higher NTU levels, even though DOC levels were highest in July therefore regardless of the DOC composition, months with similar characteristics will produce the largest sludge loads.

Site 13 currently coagulates using Alum, so comparisons need to be drawn between coagulant type and subsequent sludge production. Figure 6.15 displays calculated sludge production on the various NTU removal figures obtained during jar tests. These NTU removal rates were used further to estimate sludge production for a range of turbidity values when coagulating with Al instead, using works dose from the specific sampling day. When used as a direct comparison between coagulants, there is little difference between the two, suggesting sludge production will remain unchanged, or with a reduction on average of 15mgL^{-1}.

6.4 Discussion

Over the three sampling periods, NOM character was shown to be highly seasonally dependant, with a large increase in the HPINA content in early Autumn. Previous studies on the variation of HPI of NOM have found levels to be higher in the summer months (Scott, 2001, Sharp et al., 2006a). September DOC levels were also higher in 2008 than were recorded for the two previous years (Figure 6.1), and peaks in DOC were associated with higher levels of flow in the river Severn as recorded by The Environment Agency.

HPI content had a significant impact on the coagulation performance and subsequently the removal of DOC, UV and turbidity. The impact of HPI on coagulation performance is widely reported in scientific literature (Bose and Reckhow, 2007, Sharp et al., 2006a, Soh et al.,

2008), however results for November had a similar quantity of HPIA and HPO NOM to July, but higher doses of coagulant were needed to achieve similar removal. This therefore denotes that the HPINA content of raw waters has the most significant impact on coagulation performance and is a considerable contributor to residual DOC concentration.

The use of zeta potential for a coagulation performance indicator was shown to useful, dependant on the HPO content of raw waters. Literature on the use of zeta potential identified that the range for optimal DOC removal was far smaller than for turbidity removal (Sharp et al., 2004), which was evident in all three sampling periods where residual DOC varied notably within the optimal zeta potential range. Even at low pH, HPSEC data identified that removal of HPI organic material was poor. This poor level of interaction with ferric salts is due to the negligible charge density of HPI fractions and the presence of stable compounds such as carbohydrates (Fearing et al., 2004a, Leenher et al., 2000). If additional removal of HPI NOM was required at this site, then the use of additional removal mechanisms would need to be considered.

At different pH and coagulation doses, DBP production was generally higher with increased dose and pH. THM production was significantly lower than TTHMFP due to the mechanism of the test; THMs were fixed after 40 minutes (representative of site contact time in disinfection tank), whereas formation potential is fixed after 5 days. THMFP is representative of THM formed during the distribution system. Links between DBP formation and residual DOC concentration showed a general increase in DBP production with a rise in residual DOC. Observed scatter with the relationship was evident in September and November however. Relationships between THM and DOC are thought to

be highly seasonally dependant and site-specific, and DBP formation is influenced by low- or non-UV absorbing moieties and the presence of other DBP (Bond et al., 2009, Ates et al., 2007). The increase in HAAFP during September results is also potentially linked to the increased presence of HPINA in raw waters. Literature on HAA formation has previously linked HAA formation to the presence of amino acids and carbohydrates present in HPI NOM (Bond et al., 2009).

Site 13 cost data is based on costs for pH alteration and coagulant dose. pH changes prove to be the most influential factor, causing costs to be substantially higher for lower pH coagulation. It is inevitable that pH 4 to 5 may not be feasible on site all year round, only at times where increased removal is needed. Results showed that even a small reduction in pH would have a positive impact on NOM removal; however the most significant results were only found at pHs of 4 and 4.5. Months such as November which has a lower initial pH would prove cheaper to reduce pH so could be a more viable option for additional NOM removal at Site 13 WTW.

The WRc model used to calculate sludge is commonly used in the water industry for sludge estimation, and although the model is heavily dependent on turbidity removal, it provides reasonable approximation of sludge production and any predictive costs for coagulation would benefit from having an evaluation of sludge production. Fully representative figures would be unobtainable without a larger trial of low pH coagulation.

6.5 Conclusions

This chapter focused on objective (iv):

To establish whether current treatment conditions are capable of removing increased amounts of NOM in order to reduce DBP formation.

The work presented in this chapter identified that Site 13 WTW has the potential to significantly increase DOC removal on site irrespective of raw water quality, and removal can be accurately predicted through fluorescence and UV_{254} measurements. Seasonal changes in NOM were found to significantly impact on achievable DOC removal and the formation of potentially carcinogenic DBP.

Links between the HPINA content of NOM and the occurrence of HAAFP were identified, and the presence of HPI NOM was found to negatively impact on the formation of DBP. Additional removal of the HPI fraction needs to be investigated further, as well as relating actual THM levels through the distribution system and working back to treatment conditions to achieve a particular concentration of THM at customers tap.

Practically, costs for low pH coagulation could be high, and it would not be feasible to coagulate at pH levels of 4-5 all year round. It would not be necessary to coagulate at a pH lower than 5.5-6 however as lower pH levels are still result in residual HPI NOM. Practically, decisions also need to consider the transportation and storage of large quantities of acid on site.

Chapter 6 Figures

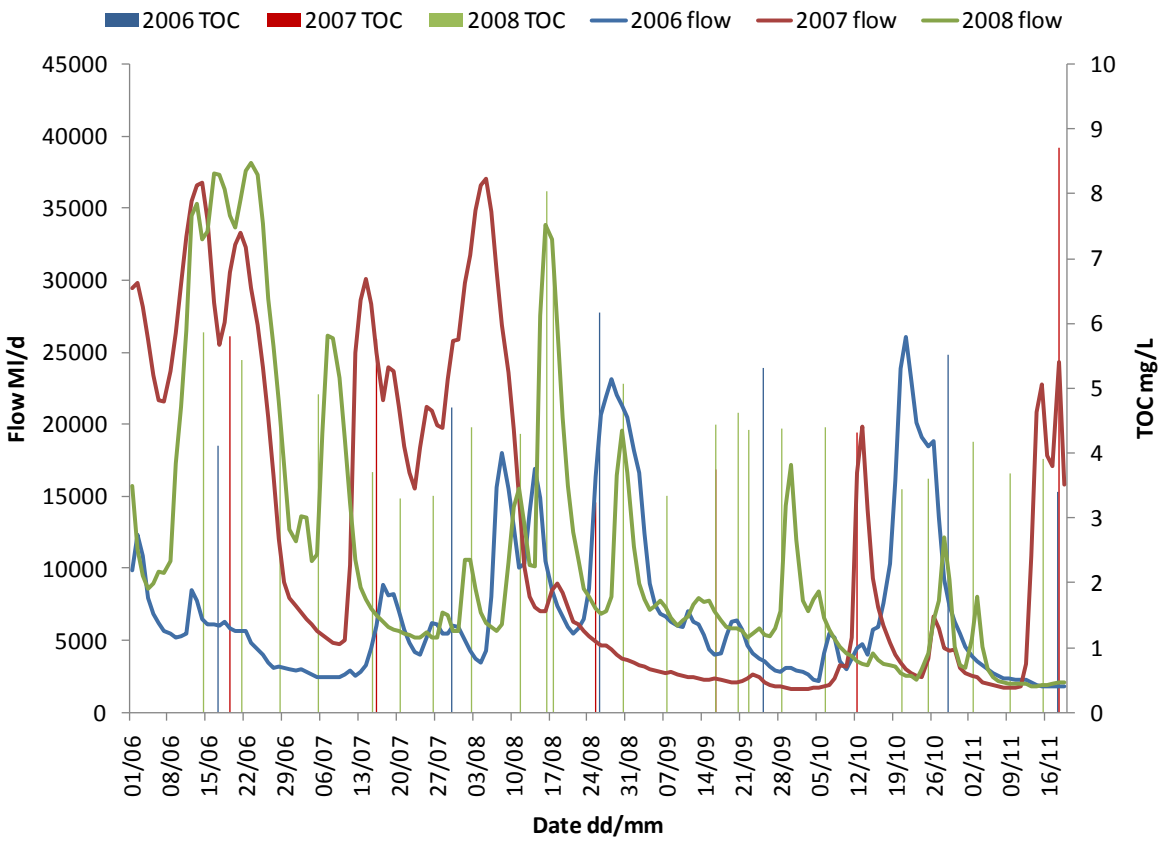


Figure 6.1 – River Severn flow data recorded downstream from Site 13 WTW, and Site 13 raw TOC data from WTW. Source; Environment Agency http://www.environment-agency.gov.uk/hiflows/station.aspx?54032

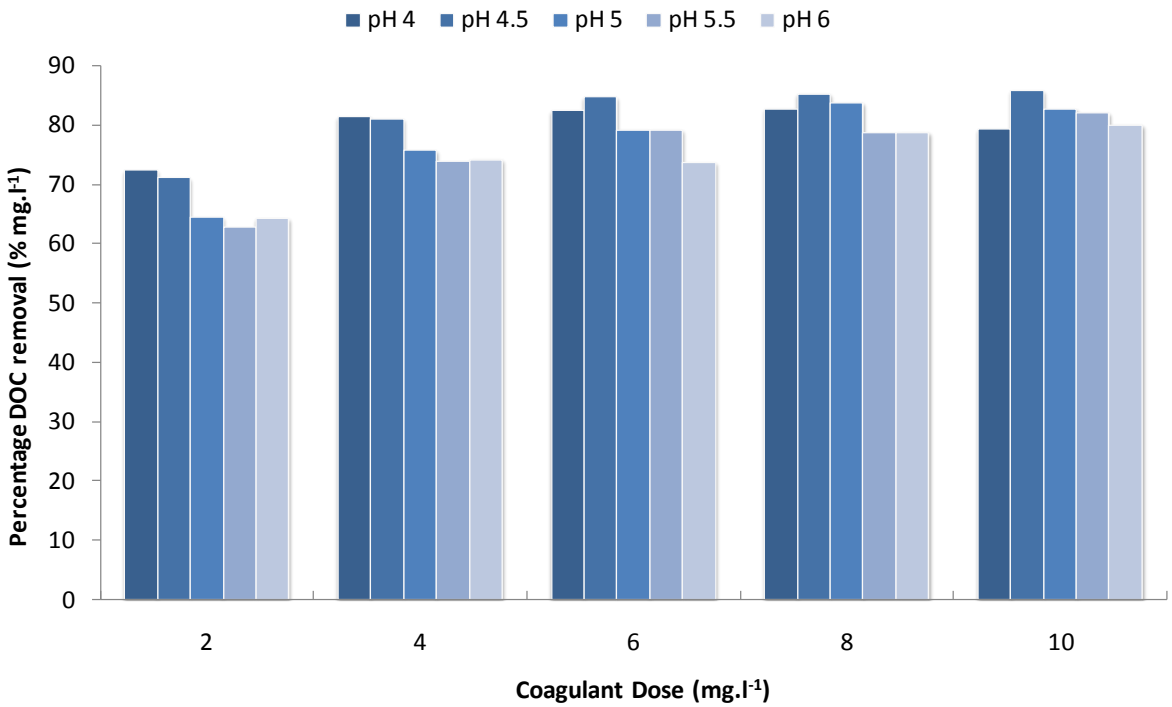


Figure 6.2a – July DOC removal

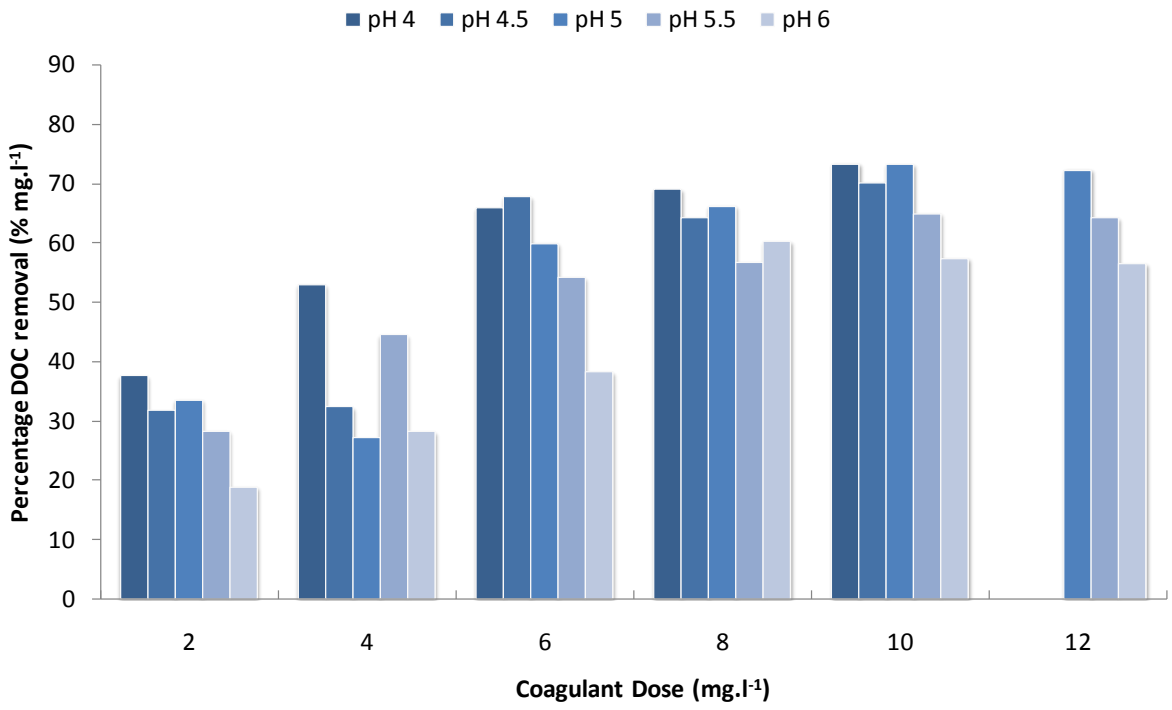


Figure 6.2b – September DOC removal

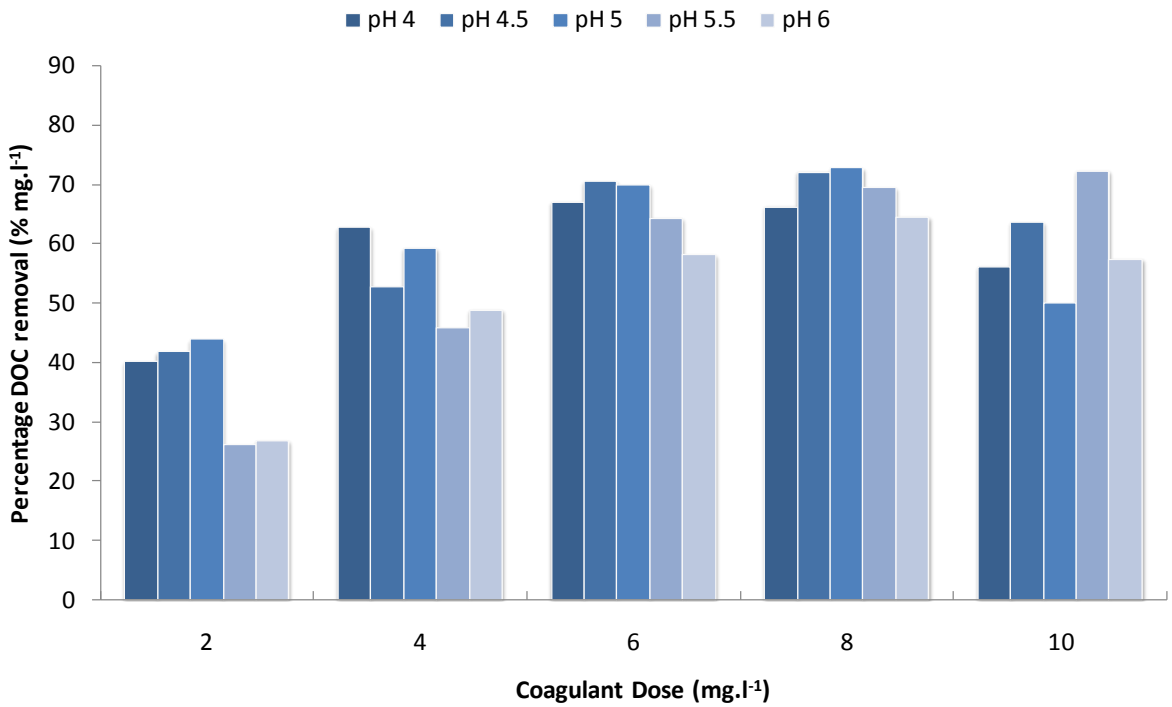


Figure 6.2c – November DOC reduction

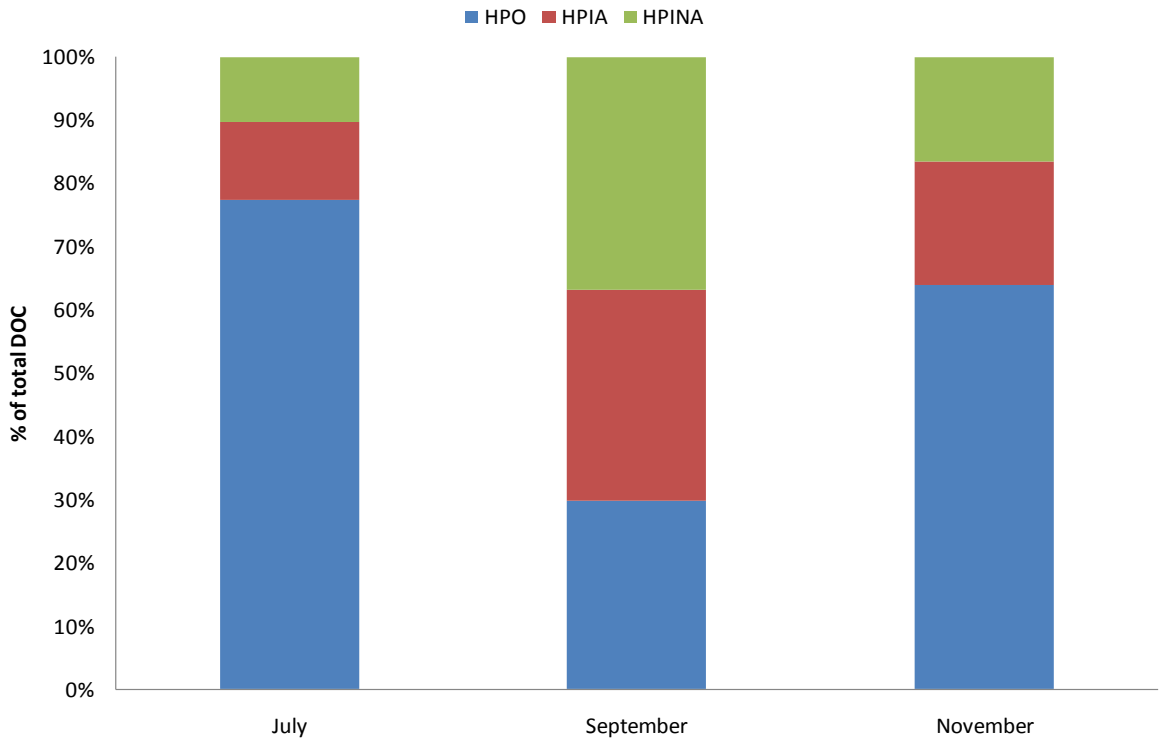


Figure 6.3 – Raw water fractions as a percentage of DOC (actual DOC of raw waters were; July, 7.6 mg.L^{-1}, September, 7.3 mg.L^{-1}, November 7.0 mg.L^{-1})

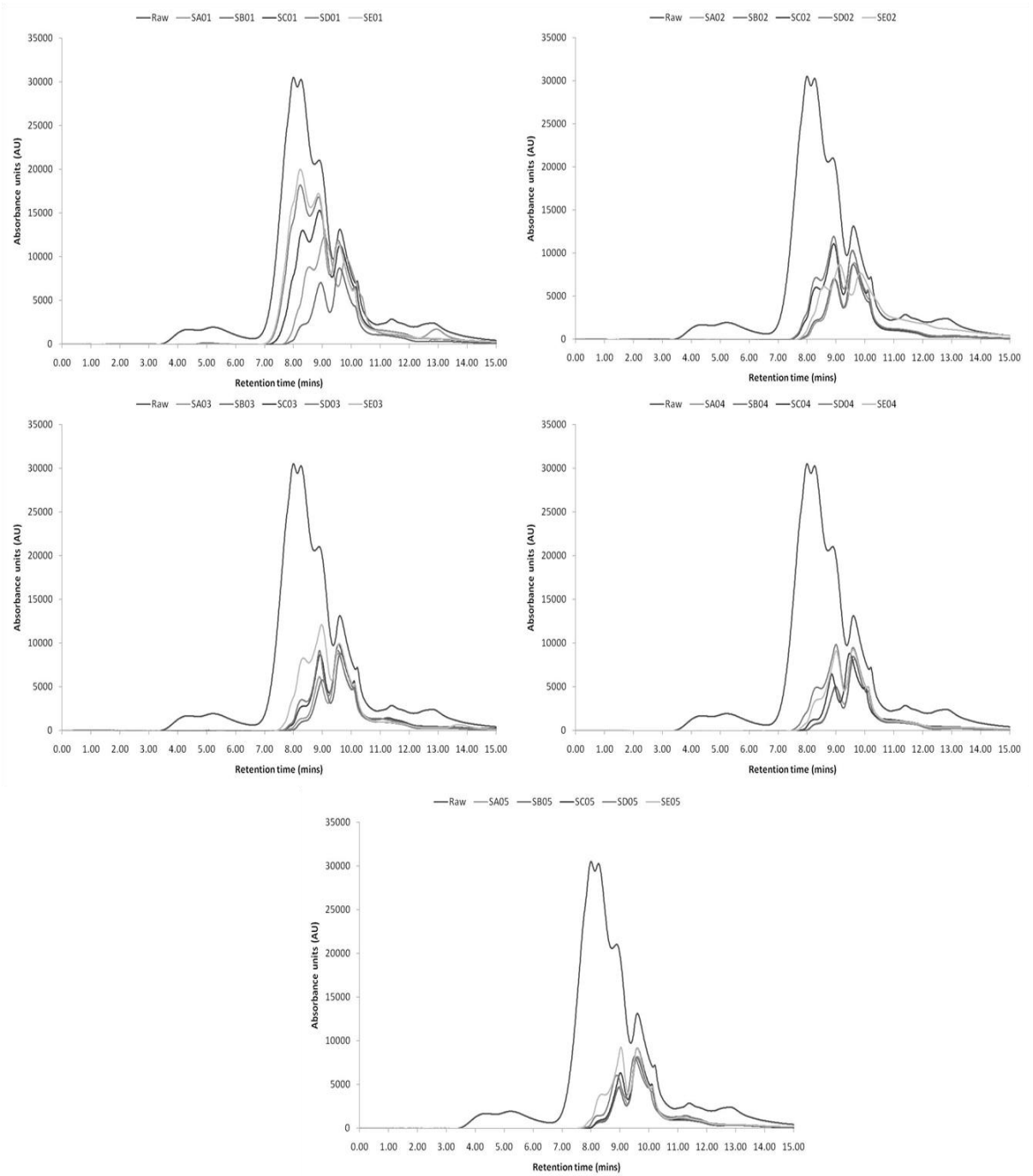


Figure 6.4 – July HPSEC chromatograph results, ordered according to coagulant dose. See table 6.1 for sample name information.

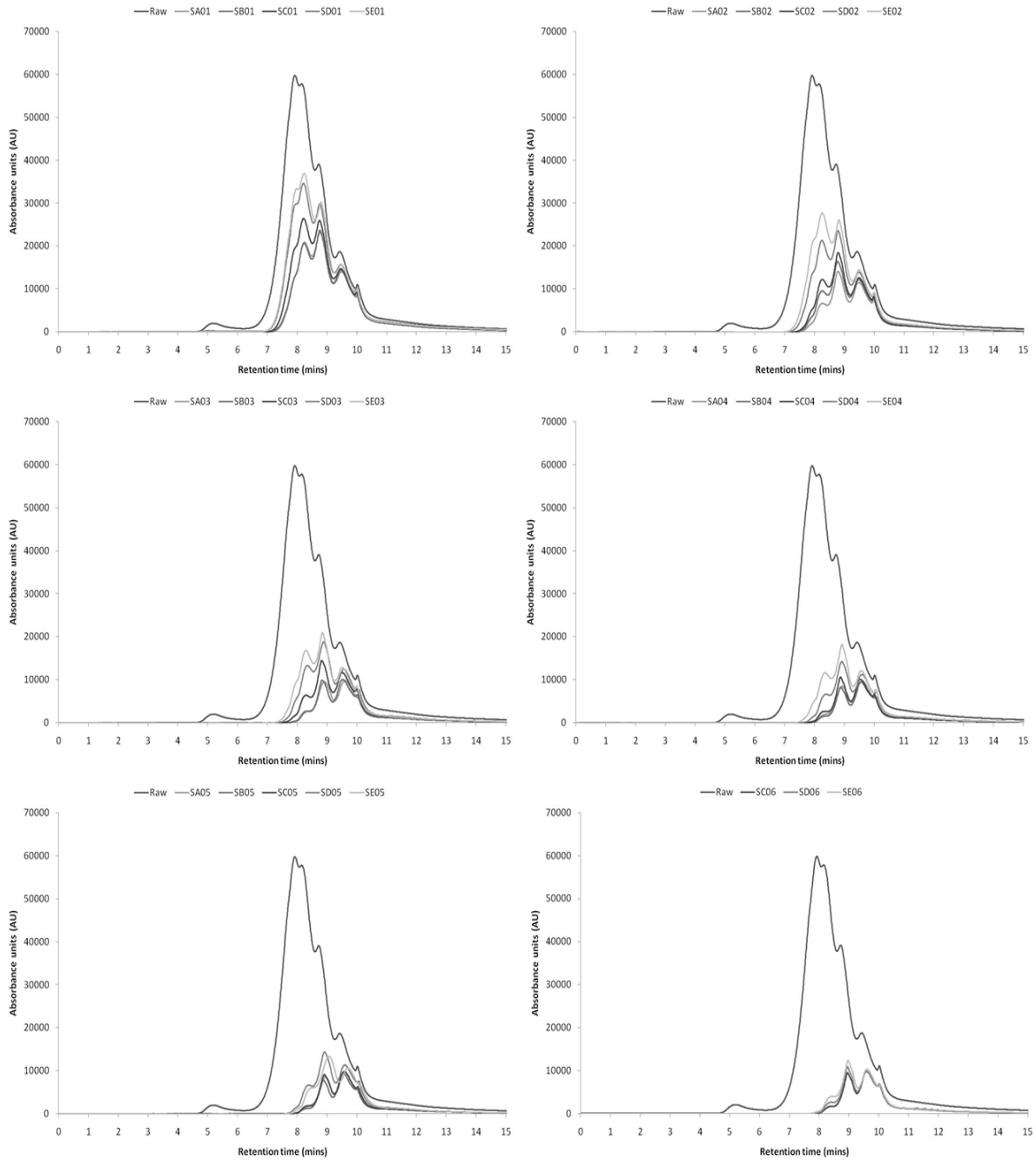


Figure 6.5 – September HPSEC profiles, ordered according to coagulant dose. See table 6.1 for sample name information.

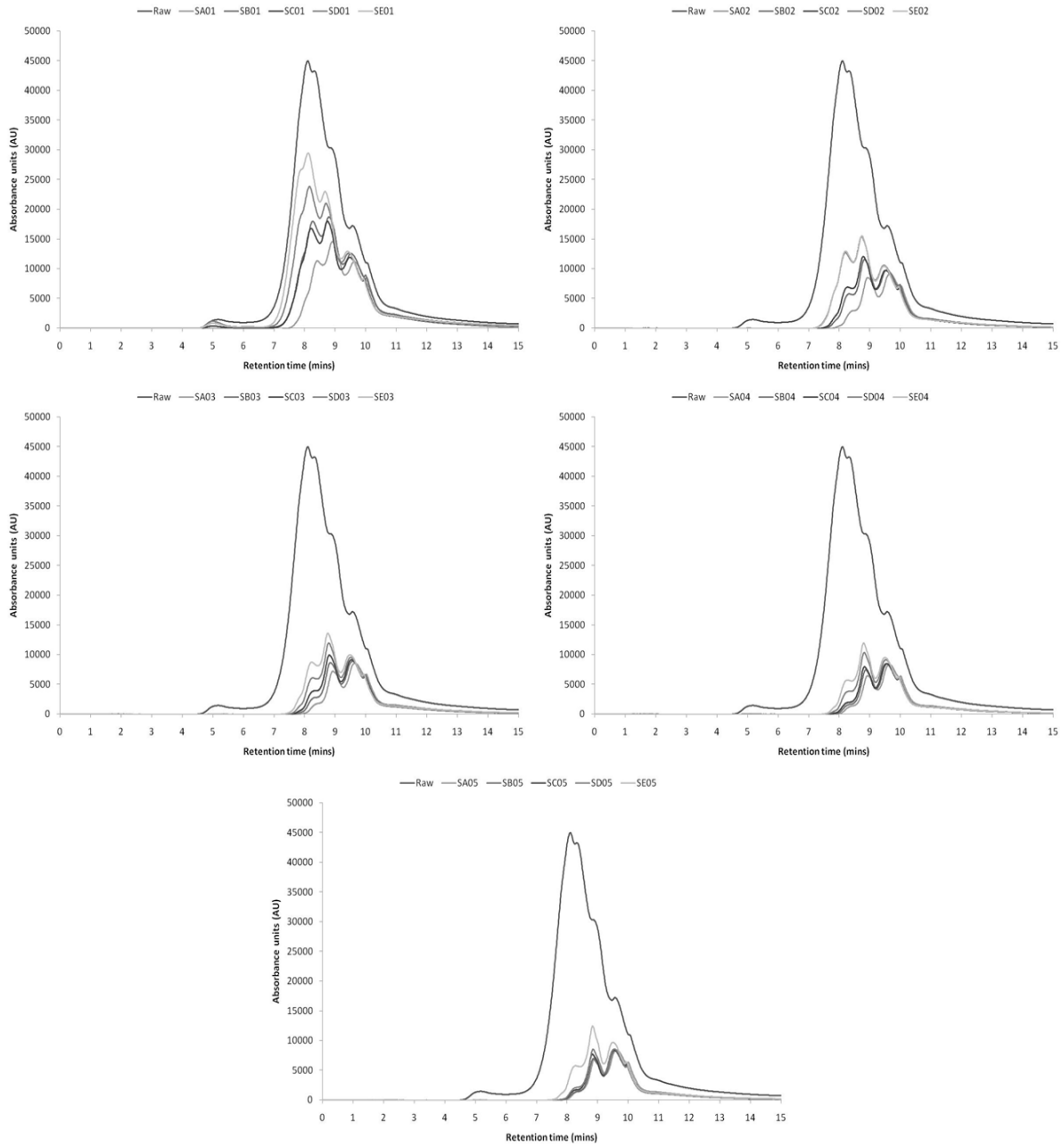


Figure 6.6 – November HPSEC profiles, ordered according to coagulant dose. See table 6.1 for sample name information.

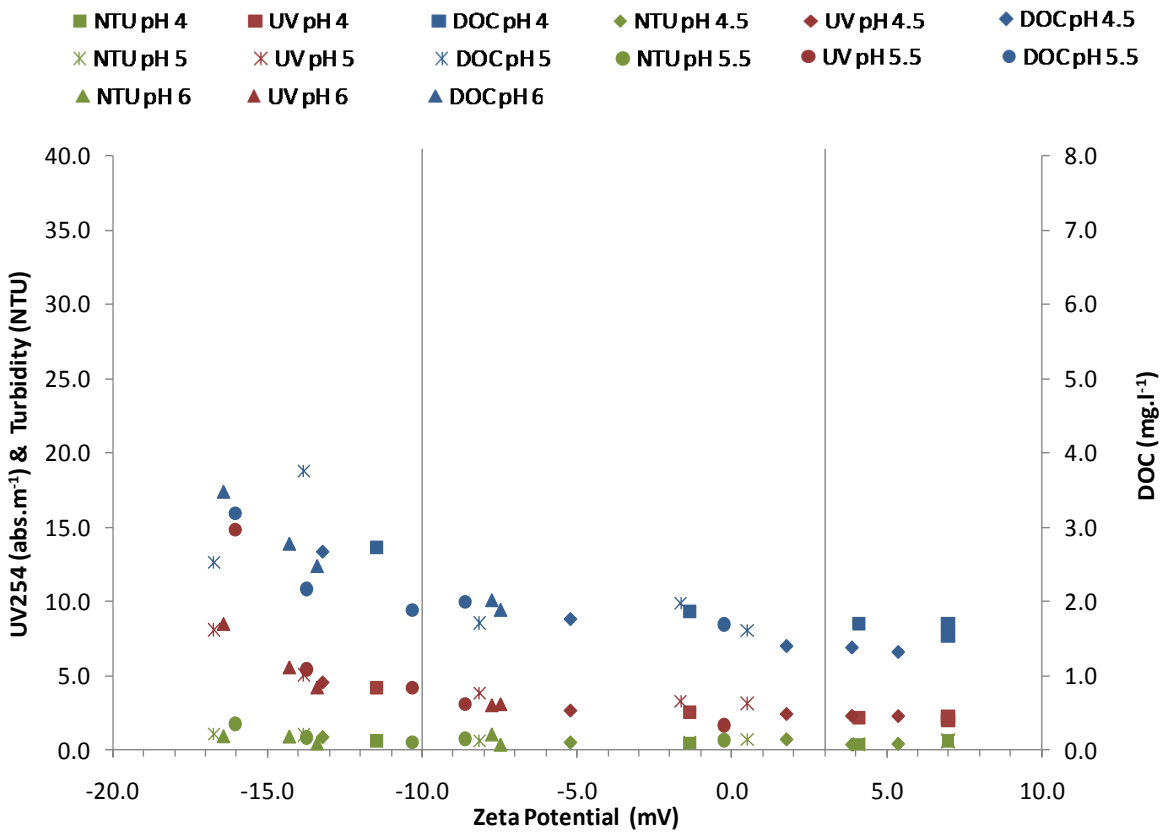


Figure 6.7a – July zeta potential measurements

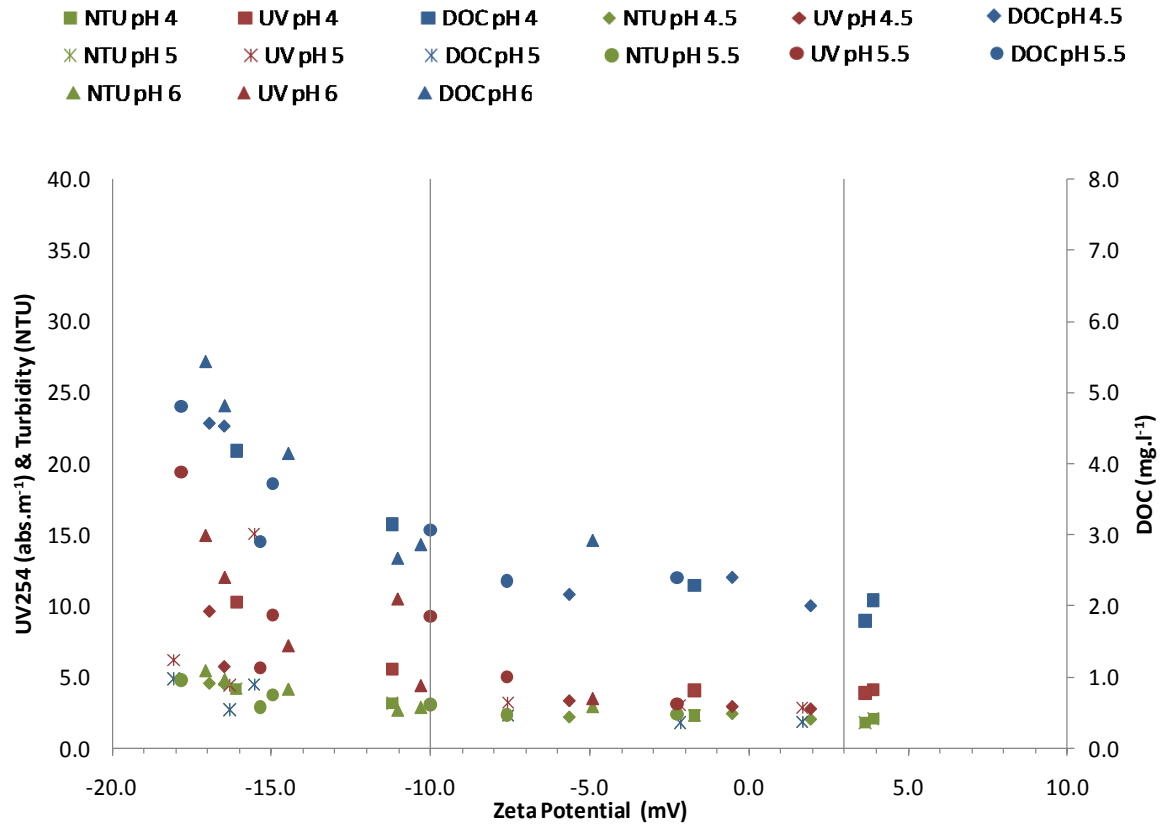


Figure 6.7b – September zeta Potential measurements

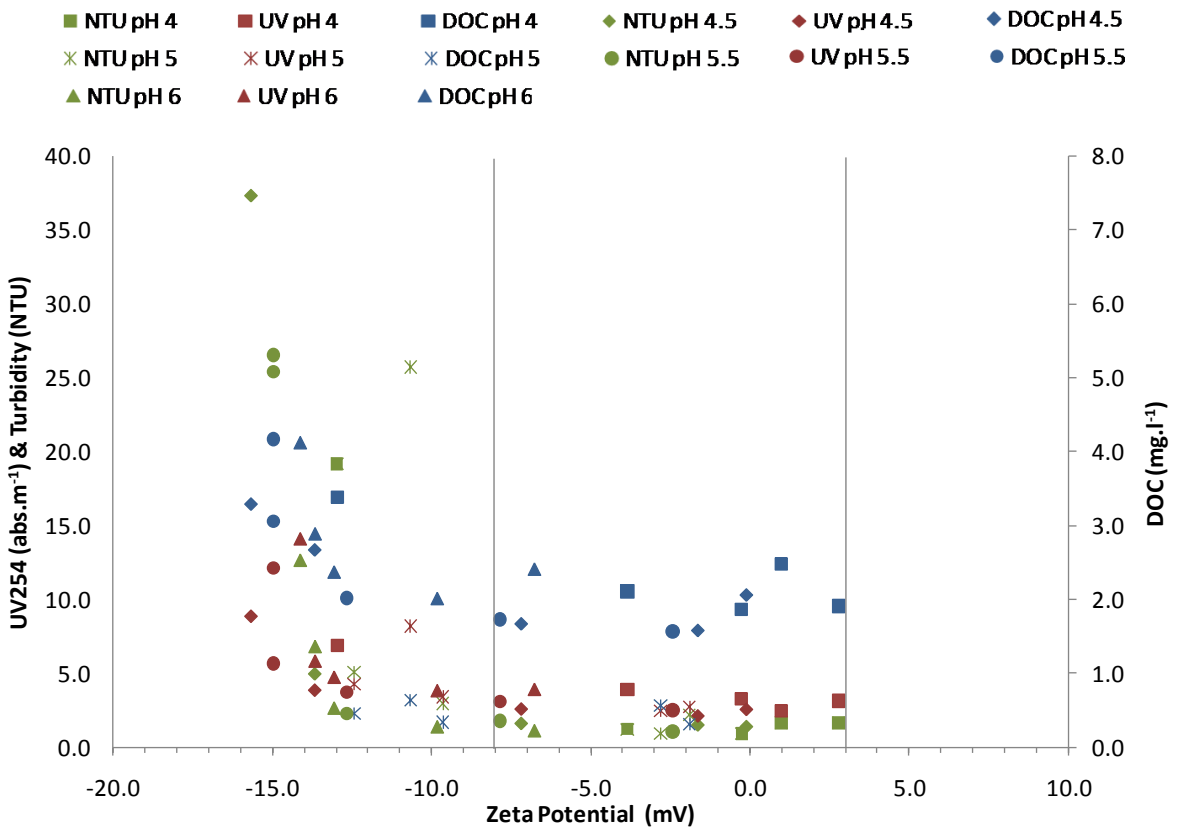


Figure 6.7c – November zeta potential measurements

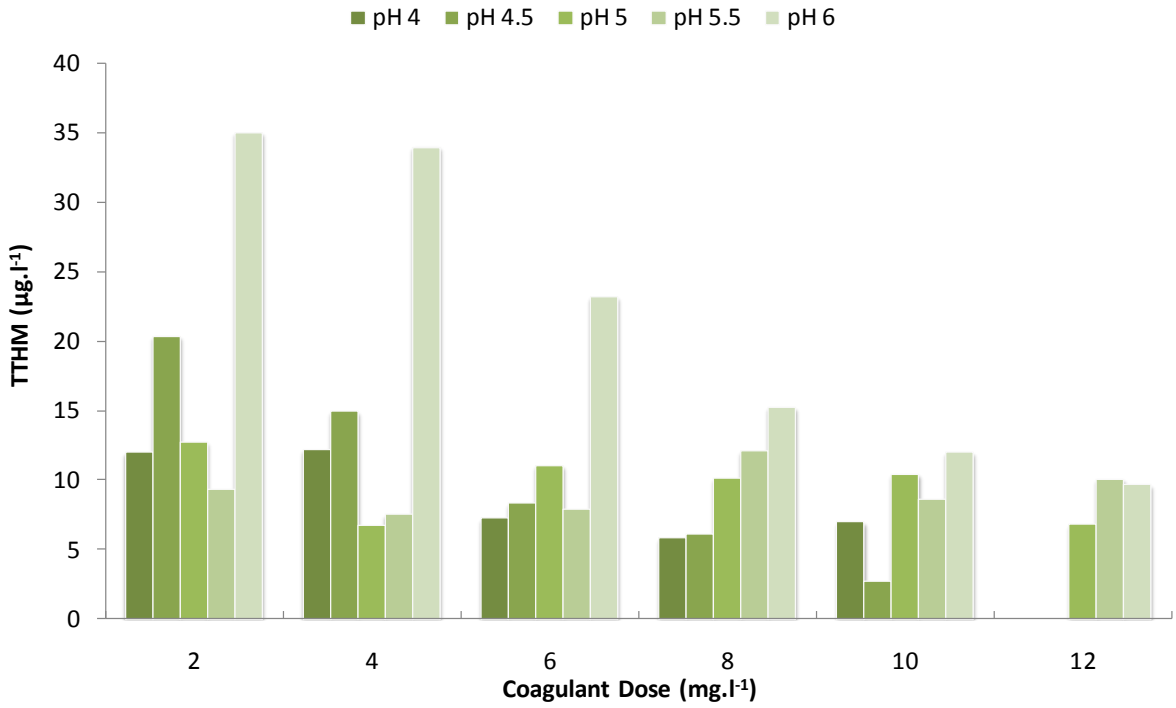


Figure 6.8a – September TTHM

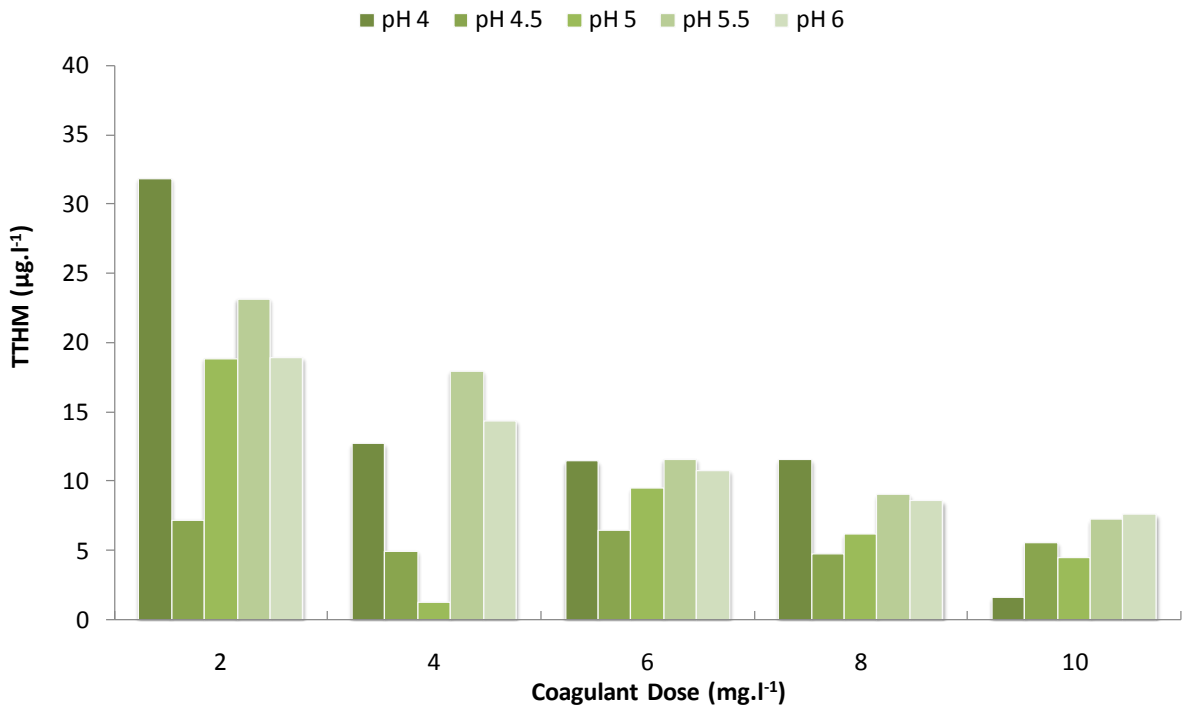


Figure 6.8b – November TTHM

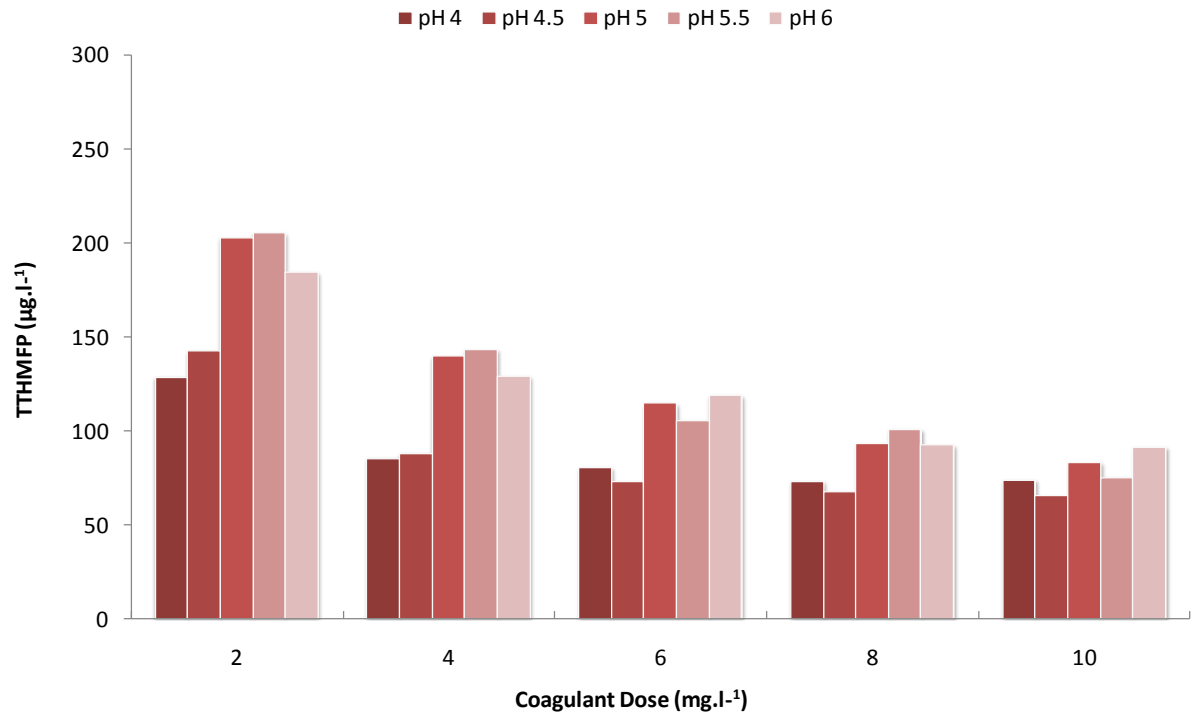


Figure 6.9a – July TTHMFP production rates

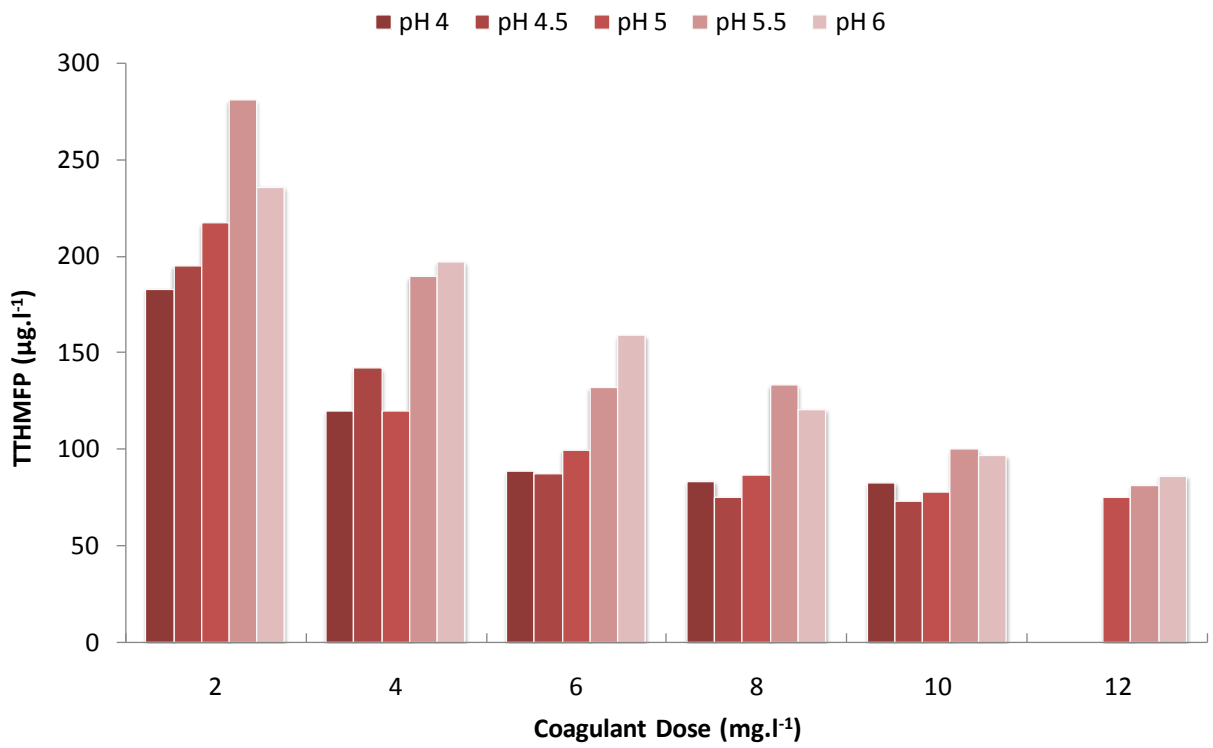


Figure 6.9b – September TTHMFP

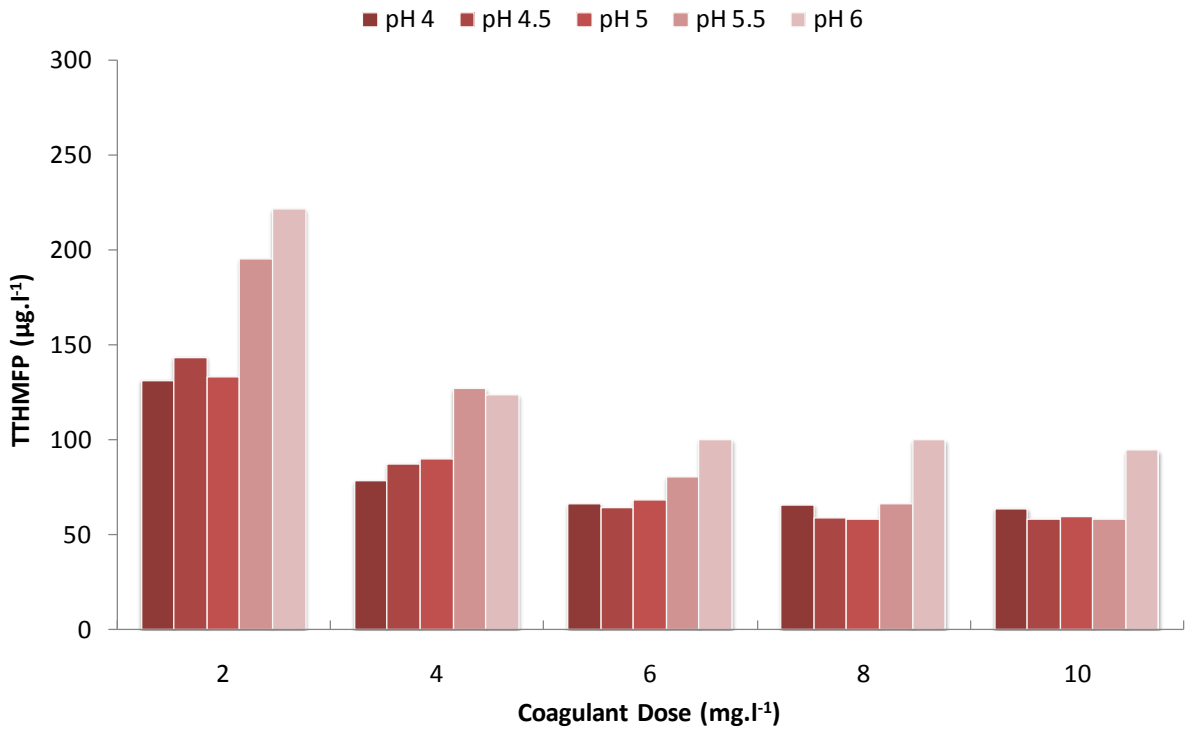


Figure 6.9c – November TTHMFP production

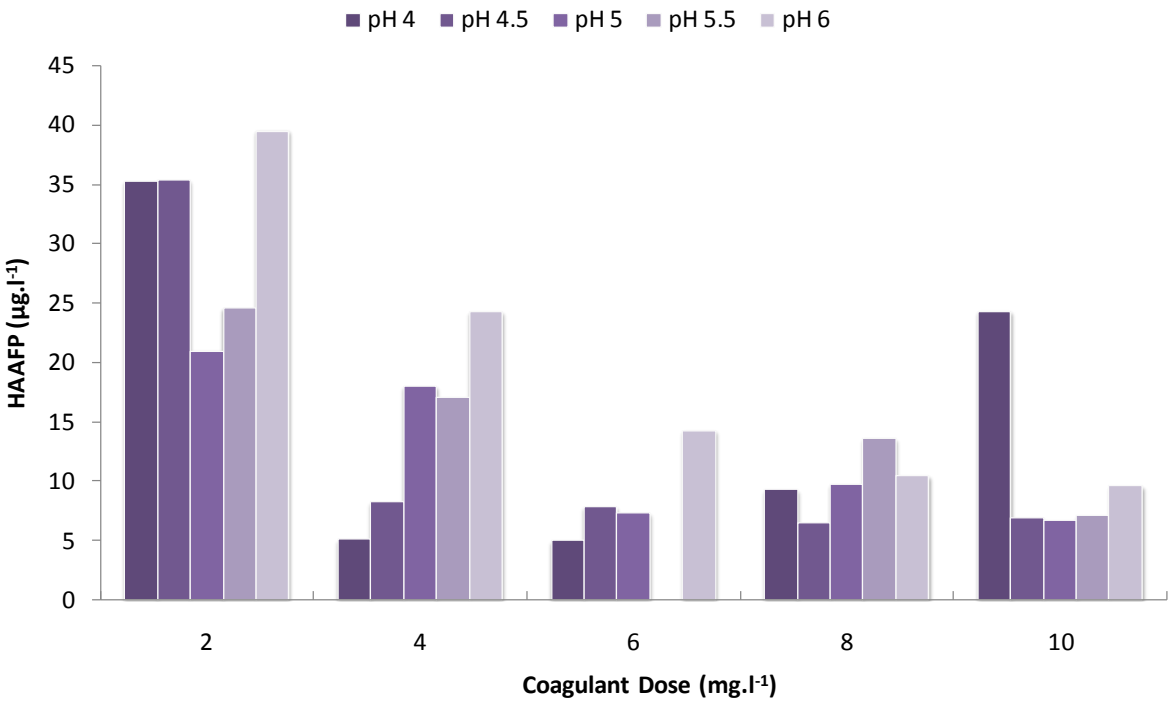


Figure 6.10a – July THAAFP production

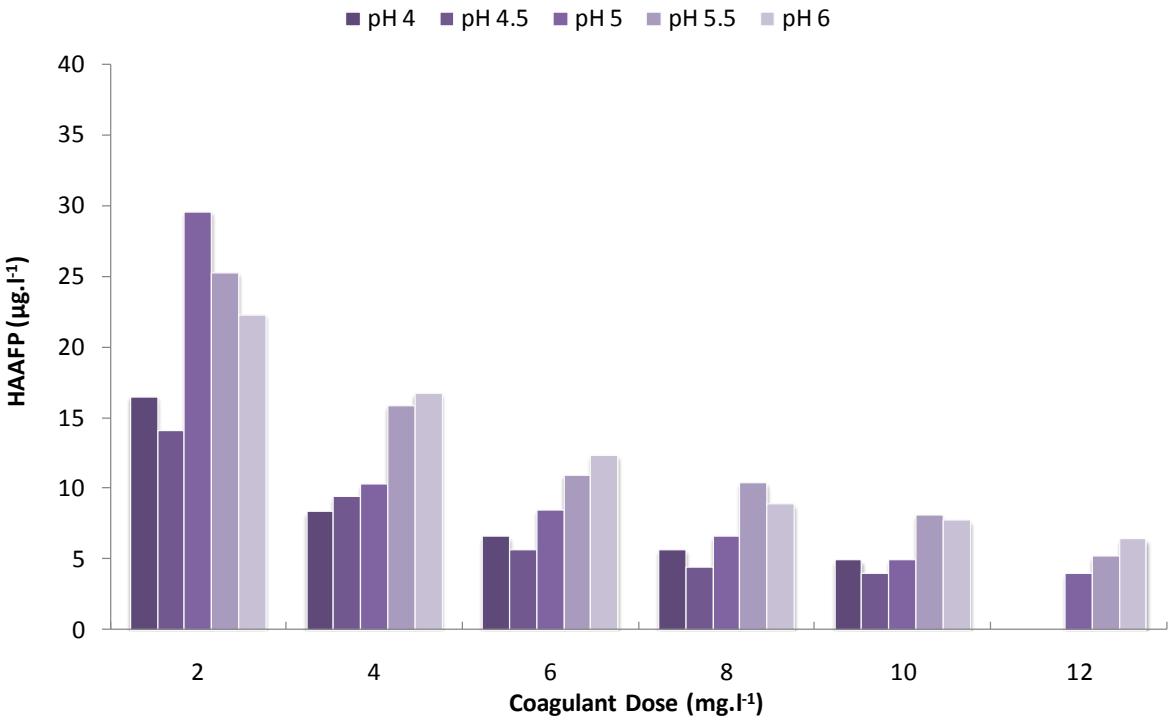


Figure 6.10b – September THAAFP

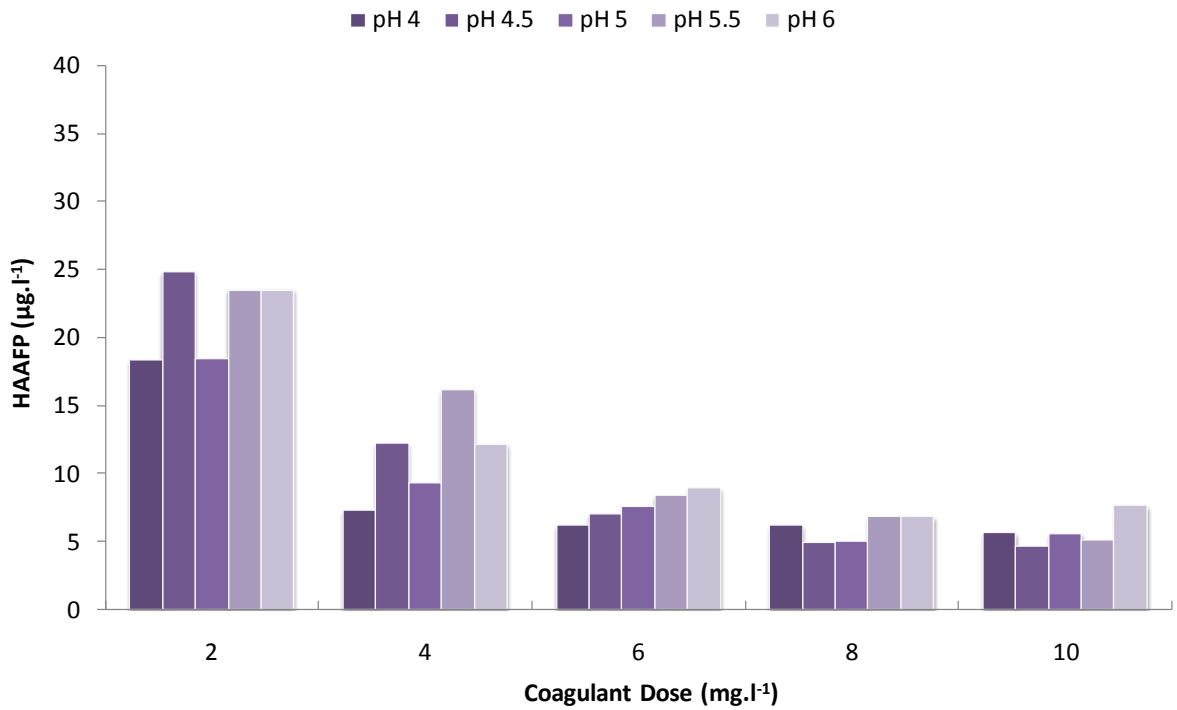


Figure 6.10c – November THAAFP production

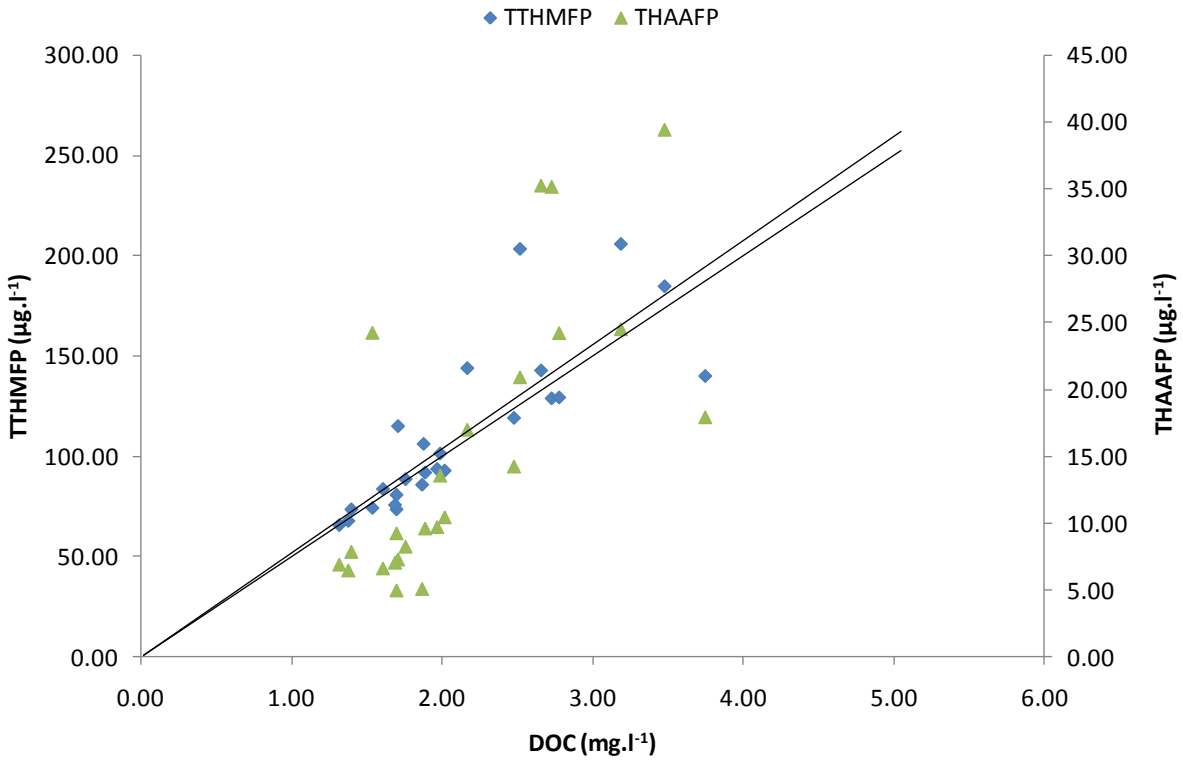


Figure 6.11a – July DBP

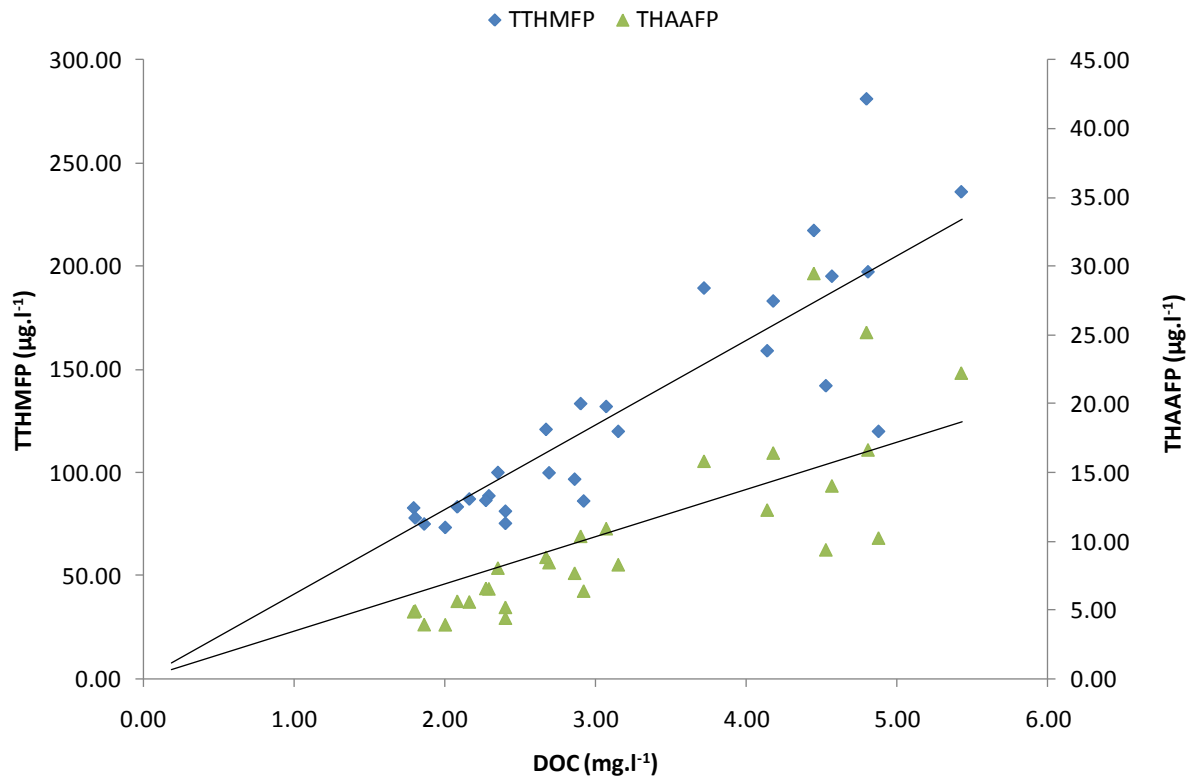


Figure 6.11b – September DBP Vs DOC correlations

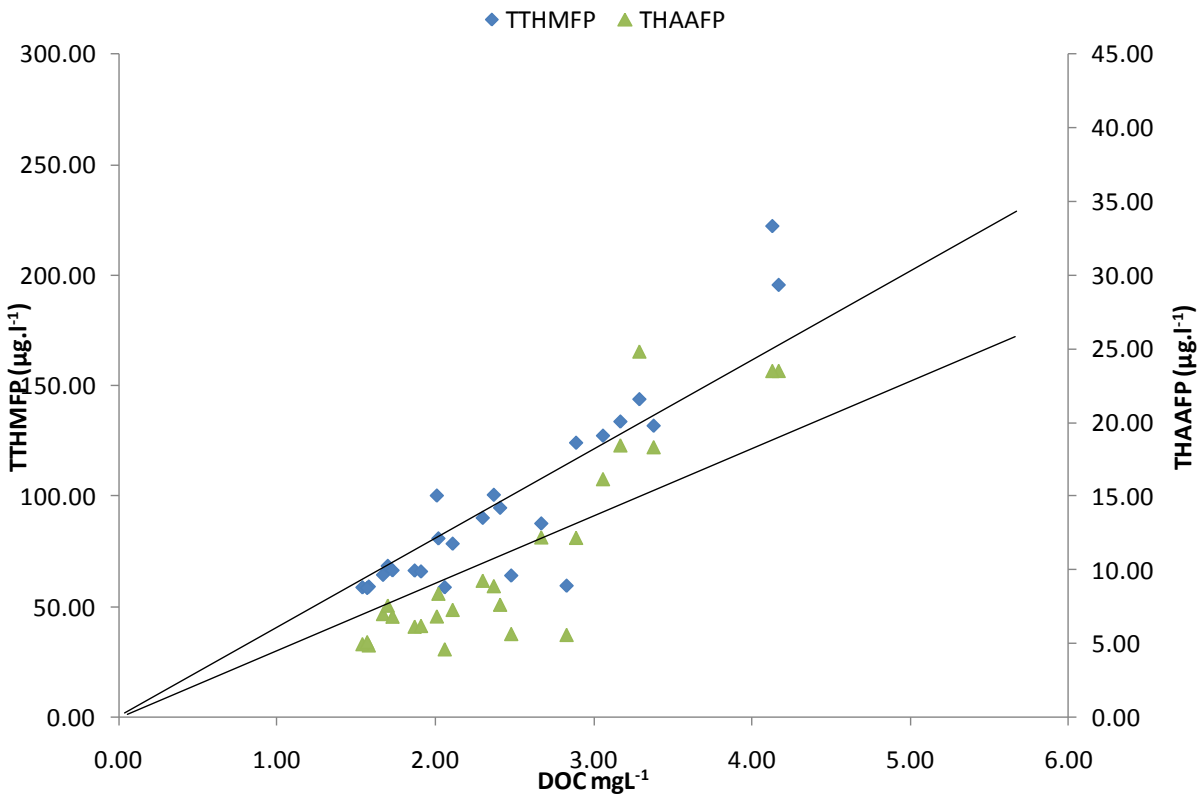


Figure 6.11c – November DBP Vs DOC

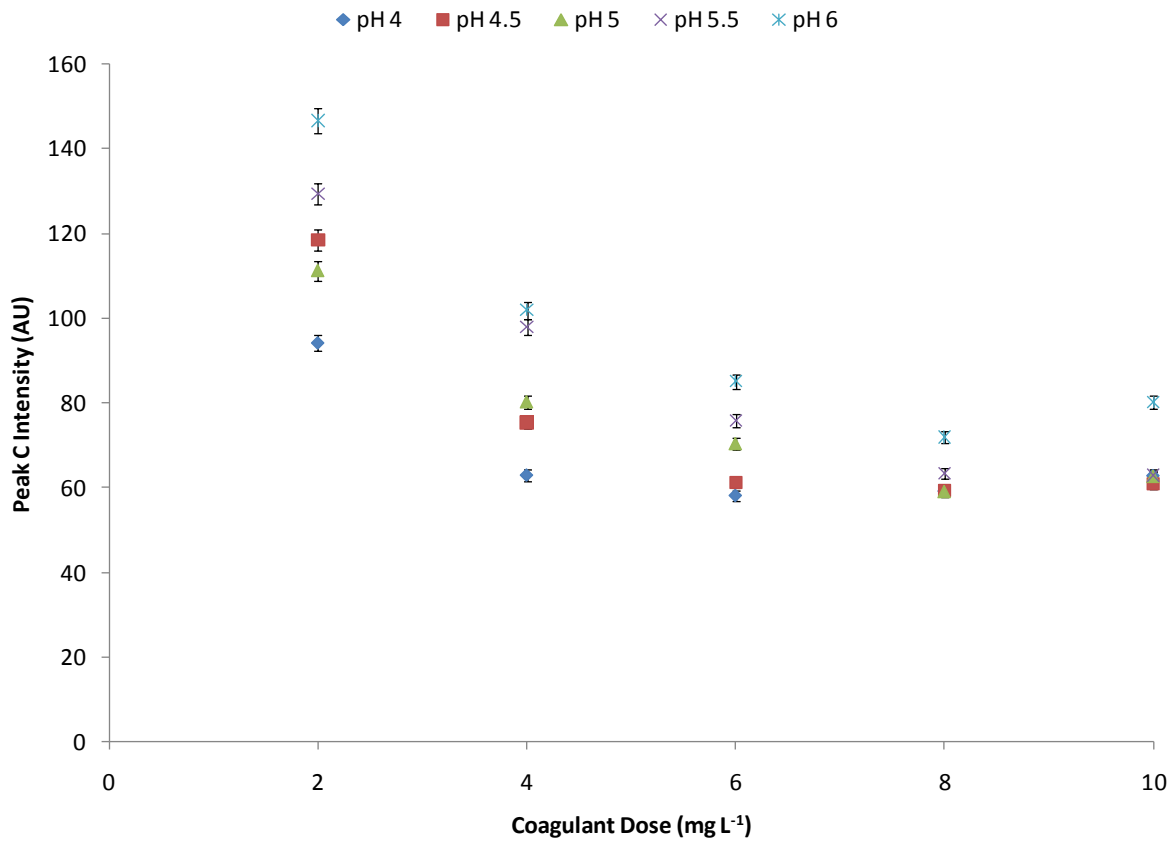


Figure 6.12a – November peak C fluorescence intensity

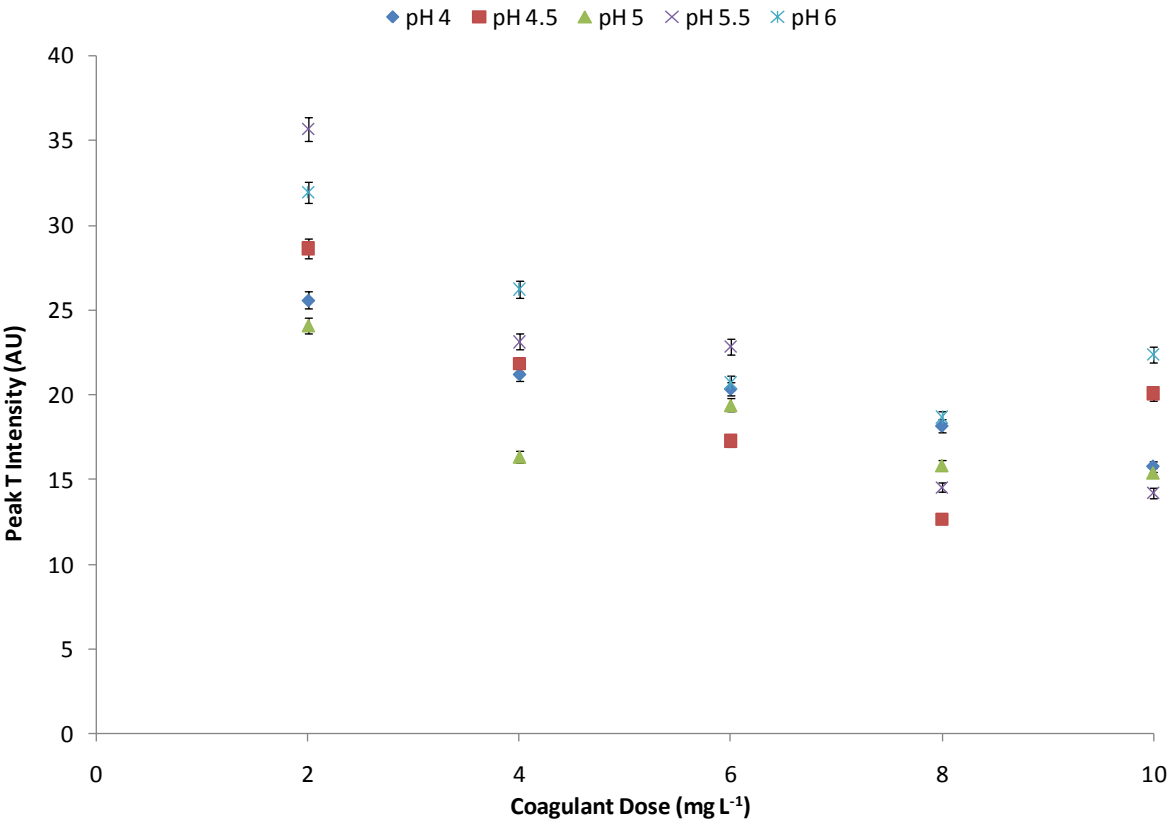


Figure 6.12b – November peak T fluorescence intensity

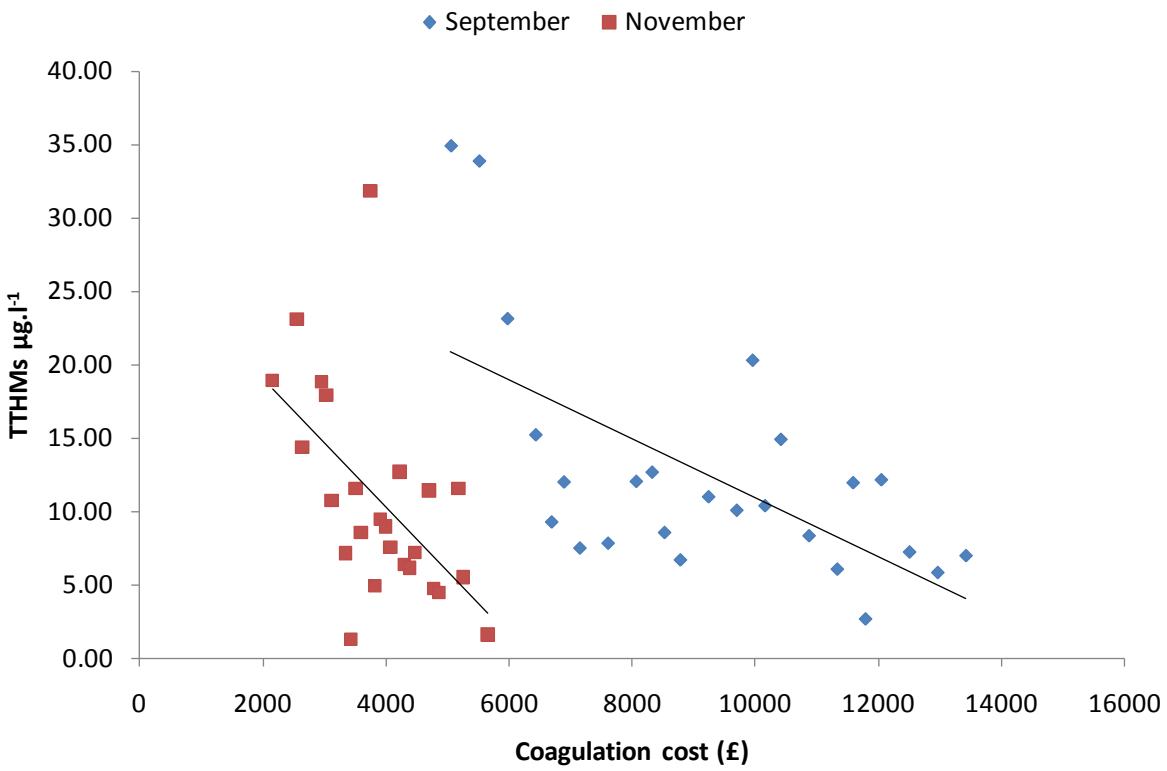


Figure 6.13a – TTHM production compared to predicted coagulation cost. Predicted coagulation cost calculated using actual WTW costs for ferric

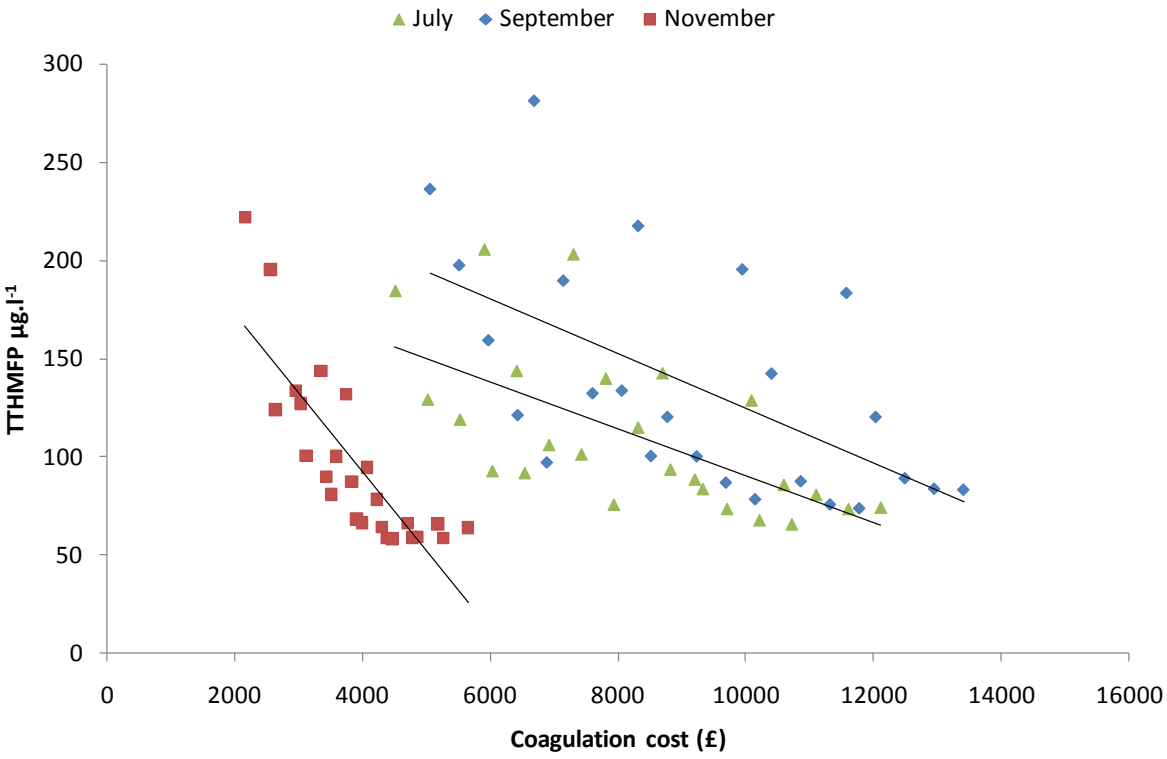


Figure 6.13b – TTHMFP production compared to predicted cost

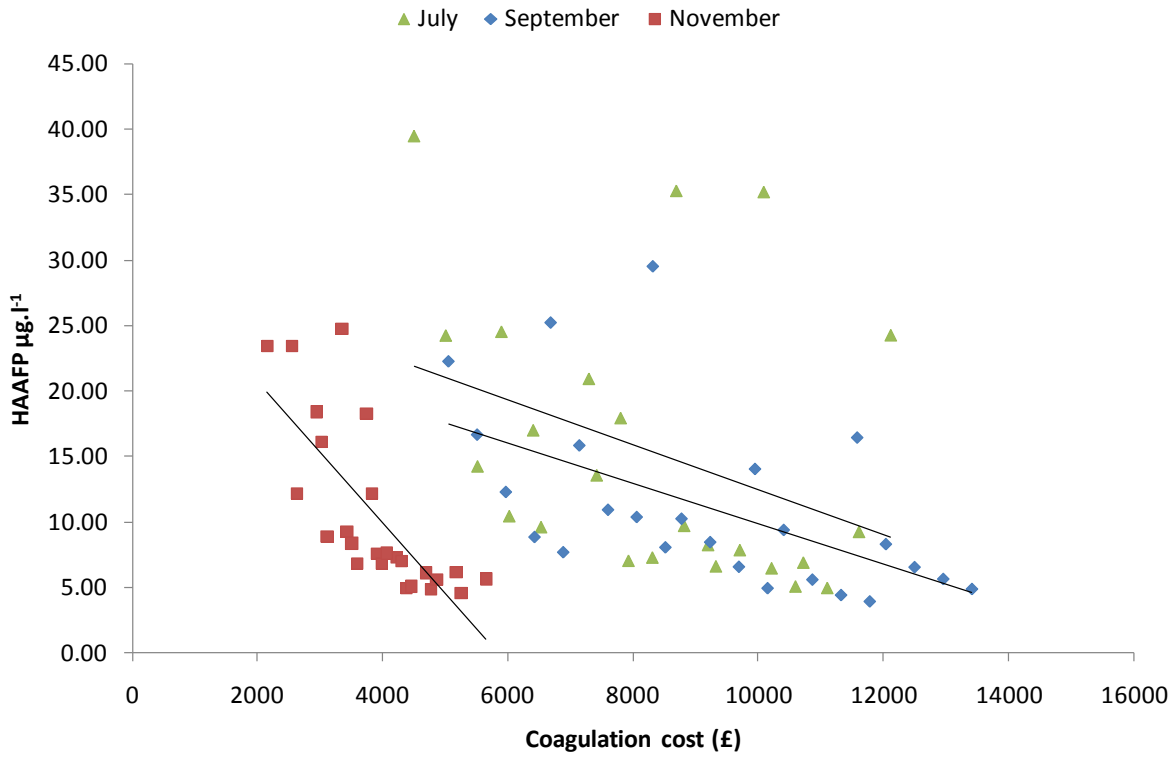


Figure 6.34c – HAAFP production comparable to predicted cost

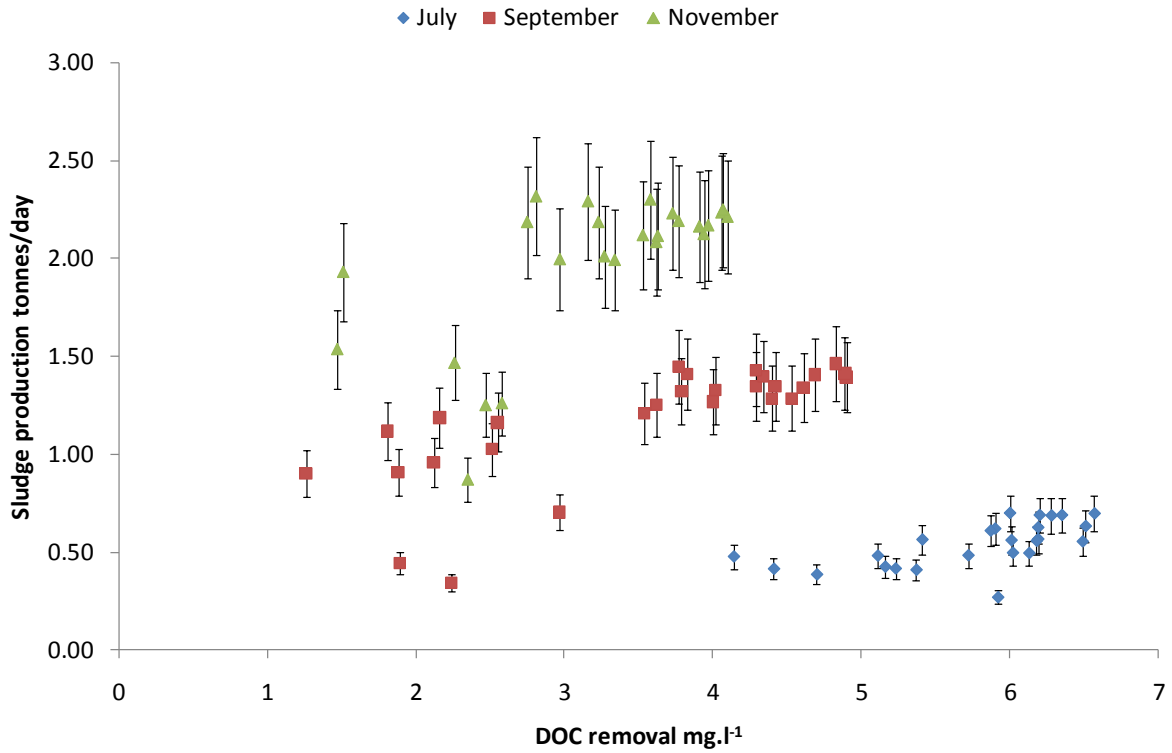


Figure 6.14 – Sludge production vs. DOC removal

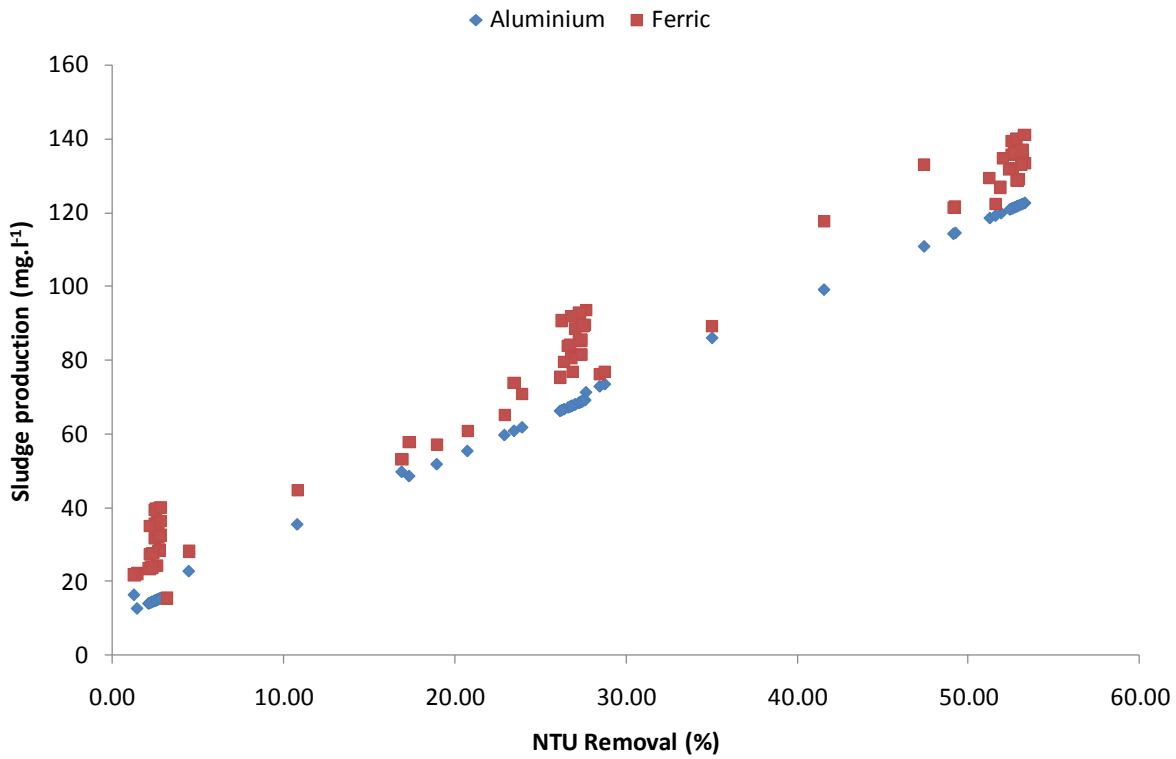


Figure 6.15 – Calculated Ferric vs. Aluminium sludge production

Chapter 6 Tables

Table 6.1 – Sample details

Sample Name	pH	Coagulant Dose $mg.l^{-1}$
SA01	4.0	2.0
SA02	4.0	4.0
SA03	4.0	6.0
SA04	4.0	8.0
SA05	4.0	10.0
SB01	4.5	2.0
SB02	4.5	4.0
SB03	4.5	6.0
SB04	4.5	8.0
SB05	4.5	10.0
SC01	5.0	2.0
SC02	5.0	4.0
SC03	5.0	6.0
SC04	5.0	8.0
SC05	5.0	10.0
SD01	5.5	2.0
SD02	5.5	4.0
SD03	5.5	6.0
SD04	5.5	8.0
SD05	5.5	10.0
SE01	6.0	2.0
SE02	6.0	4.0
SE03	6.0	6.0
SE04	6.0	8.0
SE05	6.0	10.0

Table 6.2 – Raw water characteristics

Sampling Run	Date	pH	UV_{254} (m^{-1})	Turbidity NTU	DOC mgL^{-1}
July	28th July 2009	7.6	12.3	3.2	7.9
September	15th Sept 2009	7.3	23.0	28.0	6.7
November	14th Nov 2009	7.0	19.3	54.2	5.6

Table 6.3 – July percentage HPSEC peak reduction

	pH	Coagulant Dose (mgL^{-1} Fe)	Peak I Removal (%)	Peak II Removal (%)	Peak III Removal (%)	Peak IV Removal (%)	Peak V Removal (%)
SA01	**4**	**2**	82.2	0.3	32.1	45.6	72.0
SA02	**4**	**4**	96.1	47.7	52.3	40.4	90.8
SA03	**4**	**6**	96.8	62.0	50.1	38.4	90.0
SA04	**4**	**8**	100.0	63.8	64.2	8.8	93.4
SA05	**4**	**10**	100.0	69.6	69.2	27.6	64.2
SB01	**4.5**	**2**	82.1	27.6	48.9	15.1	65.0
SB02	**4.5**	**4**	95.4	46.8	55.3	48.8	82.9
SB03	**4.5**	**6**	97.6	59.7	54.3	42.3	92.3
SB04	**4.5**	**8**	97.9	70.0	59.7	43.9	89.1
SB05	**4.5**	**10**	98.0	73.7	56.1	33.2	87.1
SC01	**5**	**2**	69.1	1.2	26.1	27.1	70.5
SC02	**5**	**4**	87.5	23.5	42.9	37.9	82.6
SC03	**5**	**6**	94.4	41.5	45.0	30.1	82.6
SC04	**5**	**8**	97.4	61.5	55.6	38.5	73.5
SC05	**5**	**10**	97.3	62.8	54.1	40.1	87.5
SD01	**5.5**	**2**	53.4	3.7	31.4	17.9	61.1
SD02	**5.5**	**4**	85.3	17.2	41.0	28.4	86.5
SD03	**5.5**	**6**	93.6	42.2	54.9	32.1	72.3
SD04	**5.5**	**8**	88.1	38.7	51.0	38.4	88.3
SD05	**5.5**	**10**	97.4	56.4	59.3	40.8	69.1
SE01	**6**	**2**	48.2	3.2	30.6	20.3	66.7
SE02	**6**	**4**	88.3	43.1	60.7	2.6	22.0
SE03	**6**	**6**	81.9	22.6	44.4	31.5	88.9
SE04	**6**	**8**	92.1	45.6	53.5	27.1	85.2
SE05	**6**	**10**	91.0	48.5	55.6	35.5	82.2

Table 6.4 – September percentage HPSEC peak reduction

	pH	Coagulant Dose (mgL^{-1} Fe)	Peak I Removal (%)	Peak II Removal (%)	Peak III Removal (%)	Peak IV Removal (%)	Peak V Removal (%)
SA01	**4**	**2**	74.8	28.6	1.5	47.6	59.4
SA02	**4**	**4**	95.0	40.4	36.2	39.0	74.7
SA03	**4**	**6**	98.5	51.2	60.5	8.7	78.1
SA04	**4**	**8**	99.1	59.1	65.7	5.8	76.5
SA05	**4**	**10**	98.9	62.7	59.7	22.1	79.0
SB01	**4.5**	**2**	75.2	33.1	-2.3	49.3	55.0
SB02	**4.5**	**4**	92.1	33.6	28.2	40.8	68.6
SB03	**4.5**	**6**	98.5	56.9	56.7	18.5	78.9
SB04	**4.5**	**8**	99.3	64.4	66.2	7.0	79.5
SB05	**4.5**	**10**	99.4	68.9	63.0	23.6	79.8
SC01	**5**	**2**	64.3	42.3	-30.4	79.9	57.7
SC02	**5**	**4**	88.7	34.2	21.7	51.3	66.3
SC03	**5**	**6**	95.6	39.6	39.0	35.6	68.3
SC04	**5**	**8**	98.4	57.7	51.7	38.6	78.3
SC05	**5**	**10**	98.9	60.8	59.6	22.9	78.7
SC06	**5**	**12**	98.9	62.6	60.3	23.7	76.9
SD01	**5.5**	**2**	48.8	29.6	-25.3	59.7	53.0
SD02	**5.5**	**4**	74.2	38.6	-5.2	69.6	62.1
SD03	**5.5**	**6**	86.7	27.9	29.0	41.9	68.1
SD04	**5.5**	**8**	95.4	32.5	48.5	23.7	71.9
SD05	**5.5**	**10**	95.4	32.7	49.7	16.0	70.5
SD06	**5.5**	**12**	98.2	56.9	58.5	27.9	79.3
SE01	**6**	**2**	43.7	20.1	-2.3	32.3	52.4
SE02	**6**	**4**	62.1	31.6	4.5	47.6	60.2
SE03	**6**	**6**	80.8	36.2	20.4	49.4	65.8
SE04	**6**	**8**	87.8	36.2	35.9	38.0	68.5
SE05	**6**	**10**	95.7	26.2	75.5	-33.9	75.0
SE06	**6**	**12**	97.2	48.2	59.0	17.3	77.1

Table 6.5 – November percentage HPSEC peak reduction

	pH	Coagulant Dose (mgL^{-1} Fe)	Peak I Removal (%)	Peak II Removal (%)	Peak III Removal (%)	Peak IV Removal (%)	Peak V Removal (%)
SA01	**4**	**2**	83.5	28.9	18.2	85.5	69.7
SA02	**4**	**4**	98.3	41.7	57.4	83.5	72.7
SA03	**4**	**6**	99.1	53.1	61.2	83.7	74.4
SA04	**4**	**8**	99.3	58.1	62.3	84.2	78.0
SA05	**4**	**10**	99.1	54.1	62.1	83.8	78.4
SB01	**4.5**	**2**	70.0	24.0	2.4	86.3	49.6
SB02	**4.5**	**4**	94.9	23.3	37.2	86.2	71.0
SB03	**4.5**	**6**	98.2	42.3	53.6	84.5	74.5
SB04	**4.5**	**8**	98.9	52.5	57.9	84.7	79.7
SB05	**4.5**	**10**	99.1	56.4	59.0	85.1	80.0
SC01	**5**	**2**	72.3	42.3	3.1	97.6	57.5
SC02	**5**	**4**	92.8	25.8	30.2	88.9	73.4
SC03	**5**	**6**	97.0	32.5	48.6	85.3	75.9
SC04	**5**	**8**	98.7	50.0	56.4	85.8	77.7
SC05	**5**	**10**	98.8	51.6	57.2	85.4	80.6
SD01	**5.5**	**2**	57.8	17.2	-7.3	88.7	48.4
SD02	**5.5**	**4**	81.3	29.0	7.4	91.3	71.2
SD03	**5.5**	**6**	94.2	23.3	39.4	87.2	75.5
SD04	**5.5**	**8**	96.9	33.2	49.9	85.6	77.8
SD05	**5.5**	**10**	98.3	45.9	58.9	84.2	81.5
SE01	**6**	**2**	42.7	-0.6	3.7	84.0	52.3
SE02	**6**	**4**	81.4	31.5	2.4	94.7	72.4
SE03	**6**	**6**	90.0	20.1	27.8	88.3	73.4
SE04	**6**	**8**	94.4	24.0	45.0	85.3	77.7
SE05	**6**	**10**	93.9	25.4	50.3	83.6	77.2

Table 6.6 – July Jar test results

Sample	pH	Coag Dose mgL^{-1} Fe	Zeta Potential mV	UV_{254} m^{-1}	Turbidity NTU	DOC mgL^{-1}	DOC Removal (%)
Raw	7.64	0	-16.5	12.3	3.2	7.9	
SA01	4	2	-11.5	4.2	0.6	2.2	72.2
SA02	4	4	-1.4	2.5	0.5	1.5	81.2
SA03	4	6	4.1	2.2	0.4	1.4	82.3
SA04	4	8	7.0	2.0	0.6	1.4	82.6
SA05	4	10	7.0	2.3	0.7	1.6	79.2
SB01	4.5	2	-13.2	4.5	0.9	2.3	71.0
SB02	4.5	4	-5.2	2.6	0.5	1.5	81.0
SB03	4.5	6	1.8	2.4	0.7	1.2	84.7
SB04	4.5	8	3.9	2.3	0.4	1.2	85.2
SB05	4.5	10	5.4	2.2	0.4	1.1	85.7
SC01	5	2	-16.7	8.1	1.1	2.8	64.4
SC02	5	4	-13.8	5.1	1.0	1.9	75.7
SC03	5	6	-8.2	3.8	0.6	1.7	79.1
SC04	5	8	-1.7	3.3		1.3	83.7
SC05	5	10	0.5	3.1	0.7	1.4	82.6
SD01	5.5	2	-16.0	14.9	1.8	3.0	62.6
SD02	5.5	4	-13.7	5.4	0.9	2.1	73.8
SD03	5.5	6	-10.3	4.2	0.5	1.7	79.1
SD04	5.5	8	-8.6	3.1	0.8	1.7	78.6
SD05	5.5	10	-0.2	1.7	0.7	1.4	82.0
SE01	6	2	-16.4	8.5	0.9	2.8	64.1
SE02	6	4	-14.3	5.6	0.9	2.1	74.0
SE03	6	6	-13.4	4.2	0.4	2.1	73.5
SE04	6	8	-7.7	3.0	1.0	1.7	78.6
SE05	6	10	-7.5	3.1	0.4	1.6	79.9

Table 6.7 – September Jar test results

Sample	pH	Coag Dose mgL^{-1} Fe	Zeta Potential mV	UV_{254} m^{-1}	Turbidity NTU	DOC mgL^{-1}	DOC Removal (%)
Raw	7.25	0	-14.2	23.0	28.0	6.7	
SA01	4	2	-16.1	10.3	5.1	4.9	37.5
SA02	4	4	-11.2	5.5	1.2	3.2	52.9
SA03	4	6	-1.7	4.1	0.7	2.3	65.8
SA04	4	8	3.9	4.1	0.8	2.1	68.9
SA05	4	10	3.7	3.9	1.0	1.8	73.2
SB01	4.5	2	-16.9	9.7	7.3	4.6	31.7
SB02	4.5	4	-16.5	5.7	1.9	4.5	32.3
SB03	4.5	6	-5.6	3.3	0.7	2.2	67.7
SB04	4.5	8	-0.5	2.9	0.6	2.4	64.1
SB05	4.5	10	1.9	2.7	0.6	2.0	70.1
SC01	5	2	-15.5	15.0	26.8	4.5	33.5
SC02	5	4	-18.1	6.2	4.1	4.9	27.1
SC03	5	6	-16.3	4.4	1.2	2.7	59.8
SC04	5	8	-7.6	3.2	0.7	2.3	66.1
SC05	5	10	-2.2	3.0	0.4	1.8	73.1
SC06	5	12	1.7	2.8	0.8	1.9	72.2
SD01	5.5	2	-17.8	19.4	23.6	4.8	28.3
SD02	5.5	4	-15.0	9.4	17.2	3.7	44.4
SD03	5.5	6	-10.0	9.3	1.7	3.1	54.1
SD04	5.5	8	-15.3	5.6	1.4	2.9	56.7
SD05	5.5	10	-7.6	5.0	1.0	2.4	64.9
SD06	5.5	12	-2.3	3.1	1.8	2.4	64.1
SE01	6	2	-17.1	14.9	9.1	5.4	18.8
SE02	6	4	-16.5	12.0	10.7	4.8	28.1
SE03	6	6	-14.5	7.2	4.6	4.1	38.1
SE04	6	8	-11.0	10.5	1.3	2.7	60.1
SE05	6	10	-10.3	4.4	0.6	2.9	57.3
SE06	6	12	-4.9	3.5	1.2	2.9	56.4

Table 6.8 – November Jar test results

Sample	pH	Coag Dose mgL^{-1} Fe	Zeta Potential mV	UV_{254} m^{-1}	Turbidity NTU	DOC mgL^{-1}	DOC Removal (%)
Raw	6.96	0	-15.8	19.3	54.2	5.6	
SA01	4	2	-13.0	6.9	19.2	3.4	40.1
SA02	4	4	-3.9	3.9	1.2	2.1	62.6
SA03	4	6	-0.3	3.3	0.9	1.9	66.8
SA04	4	8	2.8	3.1	1.6	1.9	66.1
SA05	4	10	1.0	2.5	1.7	2.5	56.0
SB01	4.5	2	-15.7	8.9	37.3	3.3	41.7
SB02	4.5	4	-13.7	3.9	5.0	2.7	52.7
SB03	4.5	6	-7.2	2.6	1.6	1.7	70.4
SB04	4.5	8	-1.7	2.1	1.5	1.6	72.1
SB05	4.5	10	-0.1	2.6	1.4	2.1	63.5
SC01	5	2	-10.7	8.2	25.7	3.2	43.8
SC02	5	4	-12.4	4.3	5.1	2.3	59.2
SC03	5	6	-9.7	3.4	3.0	1.7	69.9
SC04	5	8	-1.9	2.7	2.2	1.5	72.7
SC05	5	10	-2.8	2.4	0.9	2.8	49.8
SD01	5.5	2	-15.0	12.1	26.5	4.2	26.1
SD02	5.5	4	-15.0	5.7	25.4	3.1	45.7
SD03	5.5	6	-12.7	3.7	2.3	2.0	64.2
SD04	5.5	8	-7.9	3.1	1.8	1.7	69.3
SD05	5.5	10	-2.4	2.5	1.1	1.6	72.2
SE01	6	2	-14.1	14.1	12.6	4.1	26.8
SE02	6	4	-13.7	5.8	6.8	2.9	48.7
SE03	6	6	-13.1	4.7	2.6	2.4	58.0
SE04	6	8	-9.8	3.8	1.4	2.0	64.4
SE05	6	10	-6.8	3.9	1.1	2.4	57.3

Table 6.9 – DOC regression significance for all sampling periods. Statistically significant relationships (95 percentile) are in bold.

	TTHMFP		**TTHM**		**THAAFP**	
	R	r^2	r	r^2	r	r^2
July	0.95	0.91			0.73	0.54
September	0.90	0.81			0.84	0.71
November	0.94	0.89	0.77	0.60	0.93	0.86

Table 6.10 - November fluorescence peak C & T intensities

Sample	Peak C Intensity (AU)	Peak T Intensity (AU)	DOC $mg.l^{-1}$
Site 13 Raw	181.0	35.2	9.8
SA01	94.1	25.6	5.1
SA02	62.9	21.2	3.4
SA03	58.1	20.4	3.1
SA04	59.2	18.2	3.2
SA05	62.8	15.8	3.4
SB01	118.5	28.7	6.4
SB02	75.3	21.8	4.1
SB03	61.3	17.3	3.3
SB04	59.3	12.7	3.2
SB05	60.9	20.1	3.3
SC01	111.1	24.1	6.0
SC02	80.1	16.4	4.3
SC03	70.3	19.4	3.8
SC04	58.9	15.9	3.2
SC05	62.5	15.4	3.4
SD01	129.4	35.7	7.0
SD02	97.9	23.1	5.3
SD03	75.8	22.9	4.1
SD04	63.3	14.6	3.4
SD05	62.9	14.2	3.4
SE01	146.6	32.0	7.9
SE02	102.0	26.2	5.5
SE03	85.1	20.7	4.6
SE04	72.0	18.7	3.9
SE05	80.2	22.4	4.3

Table 6.11 – November fluorescence correlations

	Correlated Function	R	R^2
Peak C Intensity	TTHMFP	0.98	0.97
	TPBrdiCl	0.98	0.97
	TPBrdiCl, HAAFP/DOC	0.99	0.97
	CldiBr	0.77	0.60
	UV_{254}	0.98	0.96
Peak T Intensity	TPCldiBr	0.90	0.80
	TPCldiBr, UV_{254}	0.93	0.86
	TPCldiBr, TPBrdiCl	0.92	0.85

Table 6.12a – July low pH coagulation costs per Ml (£ per Ml based on 158Ml per day works production)

pH	Coagulant Dose mgL^{-1} Fe				
	2	4	6	8	10
4	63.82	67.03	70.23	73.44	76.65
4.5	54.99	58.20	61.40	64.61	67.82
5	46.16	49.37	52.58	55.78	58.99
5.5	37.34	40.54	43.75	46.95	50.16
6	28.51	31.71	34.92	38.13	41.33

Table 6.12b – September low pH coagulation costs per Ml (£ per Ml based on 143Ml per day works production)

pH	Coagulant Dose mgL^{-1} Fe				
	2	4	6	8	10
4	80.99	84.20	87.41	90.61	93.82
4.5	69.57	72.78	75.99	79.19	82.40
5	58.15	61.36	64.57	67.77	70.98
5.5	46.73	49.94	53.15	56.35	59.56
6	35.31	38.52	41.73	44.93	48.14

Table 6.12c – low pH coagulation costs per Ml (£ per Ml based on 149Ml per day works production)

pH	Coagulant Dose mgL^{-1} Fe				
	2	4	6	8	10
4	25.11	28.32	31.52	34.73	37.94
4.5	22.45	25.66	28.87	32.07	35.28
5	19.79	23.00	26.20	29.41	32.62
5.5	17.13	20.34	23.54	26.75	29.96
6	14.47	17.68	20.89	24.09	27.30

Table 6.12d – Coagulation costs at Site 13 WTW on sample days

Month	Coagulant pH	Coagulation Costs (£ per day)	THM (Final water)	TOC $mg.l^{-1}$
July	7.1	2019	27.6	2.2
September	7.2	2389	23.1	2.7
November	6.5	2522	18.5	2.6

Table 6.13 – Sludge production (coagulating using Ferric Sulphate)

Sample	pH	Coag Dose mgL^{-1} Fe	July Sludge $mg.L^{-1}$ treated water	Tonnes/day	September Sludge mgL^{-1} treated water	Tonnes/day	November Sludge mgL^{-1} treated water	Tonnes/day
SA01	4	2	24.4	0.4	65.0	1.03	89.3	1.5
SA02	4	4	28.5	0.5	76.8	1.21	129.0	2.1
SA03	4	6	32.5	0.6	81.6	1.29	133.4	2.2
SA04	4	8	35.9	0.6	85.1	1.34	135.8	2.2
SA05	4	10	39.5	0.7	88.5	1.39	139.5	2.3
SB01	5	2	23.9	0.4	60.7	0.96	53.0	0.9
SB02	5	4	28.4	0.5	75.3	1.19	121.5	2.0
SB03	5	6	31.8	0.6	81.5	1.29	132.0	2.2
SB04	5	8	36.3	0.6	85.5	1.35	136.0	2.2
SB05	5	10	40.0	0.7	89.3	1.41	140.1	2.3
SC01	5	2	23.5	0.4	21.8	0.34	76.2	1.3
SC02	5	4	27.4	0.5	70.9	1.12	121.3	2.0
SC03	5	6	32.0	0.6	80.5	1.27	129.3	2.1
SC04	5	8	15.4	0.3	85.3	1.35	134.7	2.2
SC05	5	10	39.4	0.7	89.7	1.41	141.0	2.3
SC06	5	12	n/a	n/a	92.8	1.46	n/a	n/a
SD01	6	2	22.1	0.3	28.2	0.44	93.6	1.5
SD02	6	4	27.7	0.5	44.6	0.70	76.8	1.3
SD03	6	6	32.2	0.6	79.6	1.25	126.9	2.1
SD04	6	8	35.5	0.6	83.9	1.32	131.7	2.2
SD05	6	10	39.5	0.7	88.5	1.40	136.9	2.3
SD06	6	12	n/a	n/a	90.7	1.43	n/a	n/a
SE01	6	2	23.8	0.4	57.1	0.90	117.6	1.9
SE02	6	4	27.6	0.5	57.7	0.91	133.1	2.2
SE03	6	6	32.4	0.6	73.8	1.16	122.4	2.0
SE04	6	8	34.9	0.6	84.1	1.33	128.7	2.1
SE05	6	10	40.1	0.7	89.4	1.41	133.1	2.2
SE06	6	12	n/a	n/a	91.9	1.45	n/a	n/a

Chapter 7. Carbon isotopic analysis of Surface Water Sites

7.1 Introduction

NOM characterisation has previously been confined to techniques such as XAD-resin extraction, HPSEC and UV_{254} analysis. Whilst these techniques are a well-established means of distinguishing between NOM HPI and HPO components, they are limited in their ability to determine source or age of DOC, and recent literature has raised concerns over the sensitivity of methods and possible chemical or physical alterations to NOM structure. Identification of NOM source or age could provide an insight into the potential reactivity of NOM to disinfectants and resistance to removal. Analysis of the radioactive and stable isotopes of carbon (^{13}C and ^{14}C respectively) can provide valuable information on catchment source, carbon age and estimated turnover times of organic matter in aquatic systems (Raymond and Bauer, 2001b).

Global exploration into the carbon isotopic signatures of river water has been at the centre of increased investigation in recent years, with studies by Raymond, Evans, Hood and Tipping pioneering the use of radiocarbon analysis techniques to identify sources and climatic trends in soil and riverine OM (Evans et al., 2007, Hood et al., 2009, Raymond and Bauer, 2001b, Tipping et al., 2007). Table 7.1 demonstrates recent studies on the carbon isotopes of riverine organic matter.

The work in this chapter focuses on objective (ii):

To investigate the potential for carbon isotopic analysis and environmental colloidal analysis as NOM characterisation tools, to address current characterisation needs and to identify trends with DBP formation.

In order to investigate the potential of carbon isotopic analysis for NOM characterisation, NOM from three contrasting surface water sites were analysed using carbon isotope techniques, alongside existing methods. In particular, the following research questions were posed;

- Can carbon isotope analysis identify differing characteristics in NOM composition in three contrasting surface waters?
- Can carbon isotopic analysis measure the changes in NOM character and composition from source to water treatment works?
- Can carbon isotopic analysis link NOM character to DBP formation?

To address these questions and the research objective of the thesis water samples for carbon isotope analysis were obtained from three Severn Trent surface water sites within the Midlands area of the UK, details of which are discussed Chapter 3, figure 3.1. Samples of river, reservoir and works inlet water were taken between July and August 2009, and analysed using DOC, UV_{254}, fluorescence, turbidity and carbon isotopic analysis. Further details of sampling and analysis can be seen in Chapter 3, table 3.7. Site 1 and Site 16 are typical examples of sites which exhibit opposing OM characteristics (table 7.2). As stated in earlier chapters, Site 1 is a moorland catchment with highly coloured and HPO-rich source water due to a densely vegetated catchment with peaty soils. Site 16 is a lowland catchment with a HPI-rich, colourless source water from a more urbanised catchment with

predominant arable usage. Site 8 has a less urbanised catchment with a prevailing farming influence with arable and pastures land use (Bieroza et al., 2009b). Source waters at Site 8 can be more coloured than Site 16 but NOM removal is no more successful, with both sites only averaging 10-30% total DOC removal through conventional treatment processes. All three sites have at least two reservoirs where water is stored before being treated. Figure 7.1 details the flow of source waters from river through the reservoir systems at each of the three sites.

7.2 Carbon isotopic characterisation of raw inlet water to WTW

In keeping with international practice ^{14}C results have been corrected to a $\delta^{13}C_{V\text{-}PDB}$ value of -25 ‰ using $\delta^{13}C$ of each sample and are reported as % modern ^{14}C (%mc) with $\pm 1\sigma$ level for overall analytical confidence (Stuiver and Polach, 1977, Mook and van der Plicht, 1999). Isotope ratios were corrected using the procedure outlined by Craig (Craig, 1957) and are reported in per mille notation relative to the international reference standard Vienna Pee Dee Belemnite ($‰_{VPDB}$) (Coplen, 1994). Conventional carbon ages are referred to in the text but don't depict the actual age of sample material, as samples consist of pre- and post-bomb carbon from weapons testing in the 1950s and 1960s.

Figure 7.2 illustrates that the raw inlet water at all three sites consists of pre-1957 DOM. Raw water at Site 8 has the lowest percentage modern carbon signature at 91.46 %mc, followed by Site 16 at 98.10 %mc. This indicates that at Site 8, material entering the catchment is from older carbon sources, from lower down in the soil profile. Site 1 raw inlet water has the highest percentage modern carbon NOM at 99.23 %mc, equating to NOM

with a conventional carbon age of five years (table 7.3). In 2001, Raymond et al. published findings that riverine DOC consisted of a large pool of biologically labile, ^{14}C enriched DOC and a smaller pool of biologically refractory, ^{14}C-depleted DOC. These findings however differ from riverine DOC findings, indicating that water entering WTW after reservoir storage at Site 8 and Site 16 contain a predominantly low percentage modern carbon ^{14}C pool of organic carbon composed prior to weapons testing in the 1960s, dependant on catchment usage or NOM characteristics.

According to scientific literature, ^{13}C signatures for UK plants lie between -30 to -25 ‰ (Waldron et al., 2009, Evans et al., 2007) (table 7.4). ^{13}C signatures for inlet water at Site 1 and Site 16 (figure 7.3) corroborate with these findings and lie just within the expected range for C3 plants; however inlet water for Site 8, with a ^{13}C signature of -19.30 ‰, has a ^{13}C signature that is isotopically heavier than anticipated. This signature could be produced by a mixture of C3 produced OM with C4 produced NOM, however other UK based DOC studies of surface waters have not reported values of $\delta^{13}C$ above -27 ‰. NOM at Site 8 WTW is therefore of an older NOM composition compared to the other sites. Site 8 catchment NOM consists of NOM from potentially more tropical plants and sourced from further down in the soil profile. This would be evidence of carbon stock destabilisation, which could ultimately influence treatment effectiveness. In contrast, Site 1 catchment NOM samples consist of younger NOM from plants and organic material – which is reflected by the isotopically lighter ^{13}C signature.

7.3 Changes in OM in reservoir storage

Figure 7.4 presents carbon isotope data for Site 8, Site 1 and Site 16 through their individual reservoir storage processes. Reservoir isotope signatures for Site 1 continue to consist of modern carbon and $\delta^{13}C$ within the C3 range for temperate plants as water passes through the three reservoirs, although small shifts towards isotopically heavier ^{13}C signatures and decreased percentage modern ^{14}C are observed from one reservoir to the next with Site 1 Howden DOC consisting of 103.60 %mc, decreasing to 100.89 %mc at Derwent and finally 99.23 %mc at the lowest Ladybower reservoir.

The most notable differences in carbon isotope signatures are seen in Site 16 and Site 8 reservoir waters. Site 8 Foremark and Staunton Harold ^{14}C percentage modern values decrease from 103.14 %mc in the river Wye to 91.46 %mc at Foremark and 91.01 %mc at Staunton Harold. A similar pattern is seen between Site 16 Upper and Lower Shustoke reservoirs with a decreased percentage modern carbon signature from 98.59 to 90.62 (%mc). With all sites, a pattern has emerged where a decreased percentage modern carbon ^{14}C is mirrored by a shift to an isotopically heavier ^{13}C. There are three potential explanations for the observed changes in reservoir water at sites Site 16 and Site 8: the leaching and transport of older carbon pools in low flow events; bioavailability of NOM and finally changes in land use; agricultural processes and climatic influences. In the following section, each hypothesis will be discussed in turn with reference to current literature.

The leaching and transport of older carbon pools at low flow events: It has long been established that the type and amount of NOM in surface waters varies seasonally, with

autumn flush periods having increased levels of DOC attributed mainly to variations in rainfall and evapotranspiration (Evans et al., 2007, Sharp et al., 2006d). A study by Zeigler et al., concluded DOC was most enriched in ^{13}C in late spring and summer, and Tipping et al., finding modern, low ^{13}C material dominant under high flow conditions, and the most depleted ^{13}C material derived from organic matter further down in the soil profile (Tipping et al., 2009, Ziegler and Brisco, 2004). It is therefore hypothesised that during low flow events NOM entering reservoirs is derived from further down in the soil profile and has a depleted and isotopically heavier ^{13}C signature.

Bioavailability of NOM: An additional explanation relates to the bacterial utilisation and bioavailability of NOM. Investigations by Raymond et al., (2001) found bacteria preferentially utilize a ^{14}C enriched (i.e. young) DOC fraction, which consequently lead to ^{14}C depleted surface water systems. However, this does little to account for shifts in ^{13}C signatures. Hood et al. (2009) also describes how relatively unaltered younger organic matter is preferentially metabolized by aquatic hetertorophs and bacteria opposed to the heavier, older and modified material. This leaves reservoir water consisting of predominantly older organic material (Hood et al., 2009, Raymond and Bauer, 2001a). The transition of younger to older carbon through the reservoirs at the three sites be attributed to younger carbon entering upper reservoirs from catchment rivers (as seen in river carbon isotope samples), being preferentially consumed by bacteria in the upper reservoirs, leaving older carbon passing through to the lower reservoirs and into WTW.

A final potential explanation regards changes in land use, climatic changes and agricultural processes. Increased DOC concentrations in many upland sources and losses of carbon in

organic-rich soils in England and Wales is a perceived consequence of climatic warming influencing the stability of soil carbon stocks (Tipping et al., 2007). Coupled with agricultural soil losses from intensively managed soils, additional carbon released into reservoirs could be sourced from further down the soil profile than previously anticipated, especially from catchments such as Site 8 and Site 16 where agriculture dominates land use patterns (Evans et al., 2007). NOM from lower down in the soil profile will be older (with a decreased ^{14}C signature) and have a depleted ^{13}C signature, and an increased intensity of agricultural processes within a catchment will release these carbon stocks into the surface waters, and subsequently to water treatment processes.

It is feasible that all three factors will be contributable to the changes in carbon signatures through reservoirs, however the extent of which each factor impacts on the carbon in surface waters will depend on the land use of the catchment.

7.4 Comparison with existing NOM characterisation techniques

Existing NOM characterisation techniques such as DOC, UV_{254} and turbidity (table 7.5) indicate settling of organic material through the reservoirs, with decreased colour, TOC and turbidity. Peak C intensity closely mirrors TOC results at all sites except Site 16 upper and lower Shustoke. Elevated turbidity, UV, TOC and fluorescence peaks T and C intensity in Site 16 inlet water points towards the re-suspension of NOM with the transference to the works for treatment. The Site 16 Shustoke reservoirs are substantially smaller than reservoirs at Site 8 and Site 1 so a degree of re-suspension of NOM is to be anticipated. The lower Shustoke reservoir is the main storage facility at Site 16, so the increased ^{14}C %mc and

heavier ^{13}C signature suggests younger allochthonous NOM is still present in reservoir waters.

Stepwise regression relationships between carbon isotope data and conventional characterisation data are shown in table 7.5. A lack of statistical relationships between the majority of the different characterisation techniques confirm existing practices are unable to provide an insight into carbon age and source. Figures 7.5 and 7.6 demonstrate a visible trend between peak C emission and ^{14}C % modern carbon and ^{13}C signatures, with decreased peak C intensity values having isotopically heavier ^{13}C signatures and lower ^{14}C percentage modern carbon. Due to the nature of the source waters, all Site 1 samples and the Site 8 river water sample have the higher peak C intensity values. Peak C emission could be a potential indicator between NOM source and age however this is an area for further investigation due to the small number of samples.

7.5 Comparisons between reservoir NOM carbon isotopic signatures and THM

THM measurements for all sites are shown in figure 7.7, and were taken after 30 and 60 minute intervals. The additional 30 minutes reaction time produces a higher THM content at all three sites. Comparisons between carbon isotopes and THM for all sites produce no obvious trends, however there is clustering shown within sites, especially between $\delta^{13}C$ and TTHM. A potential trend exists between $\delta^{13}C$ and the coefficient of proportionality, K_{TC} (an indicator of the TTHM productivity of the water) for potential formation of THM in isotopically heavier organic carbon.

When comparing the formation of TTHM at the three sites however, and the change in formation between reservoirs, at all three reservoirs there is an increased level of THM formation in the lower reservoirs. Figure 7.8 illustrates how THM formation at Site 8 and Site 1 sites are actually very similar, whereas Site 5 has the lowest level of THM formation – which could be linked to the higher levels of humic and fulvic material in the samples (Jung and Son, 2008). This increase in THM formation in the lower reservoirs again could potentially be linked to the older and isotopically heavier organic carbon present in the surface waters.

7.6 Discussion

Carbon isotopic analysis of NOM samples showed riverine NOM consists of younger carbon from C3 plants. These findings corroborated with existing carbon isotope investigations of UK riverine carbon (Evans et al., 2007, Guo and Macdonald, 2006). Isotopic analysis of NOM in subsequent reservoir storage however showed at all three sites storage lead to an isotopically heavier ^{13}C signature and decreased percentage modern carbon ^{14}C signature. The most noticeable differences were observed at Site 16 and Site 8, sites which are characterised by poor NOM removal through treatment, attributed to a high HPI NOM content.

Three potential explanations for the shifts in carbon isotope signatures were proposed, the first of which being the leaching and transport of older organic carbon from catchments in low flow events. Leaching of NOM containing older carbon could decrease ^{14}C percentage modern signatures and provide shifts towards isotopically heavier ^{13}C signatures. Research

by Tipping et al., (2009) and Ziegler and Brisco, 2004) demonstrated how the isotopic character of organic material changes with high and low flow events, with the first study by Tipping et al., (2009) specifically looking at UK samples. This is a highly plausible explanation for the noted shifts in age and composition of carbon isotopes see at Site 1 and Site 5, however, at Site 8 an input of carbon from C4 plants would only be sufficient to cause such a large shift towards an isotopically heavier ^{13}C signature such was the significance of the shift towards a heavier ^{13}C signature.

A second potential explanation regarded the preferential utilization of younger, more labile NOM by bacteria. This would lead to depletion in ^{14}C in surface waters but would not result in altering the ^{13}C signature. Recent research has also highlighted that most organisms release DOC, which would subsequently increase DOC levels in surface waters (Henderson et al., 2008). The released DOC by such organisms would have little effect on the ^{14}C levels however as any DOC released would be young carbon and could not attribute to the older carbon signatures that were found. ^{13}C would also remain unaltered, as this would depend on the type of organic material used as a food source, which would presumably be organic material within the surface water.

The final proposed explanation was an increase in the released carbon through the destabilisation of soil carbon stocks as a result of climate change and an intensification of agricultural processes. Research by Evans *et al.* (2007) concluded that climatic influences would not be accountable for such large increases of carbon in surface waters, however intensification of agricultural processes is attributable to the release of older carbon pools in soil. Research on surface water carbon isotopes frequently highlighted land use changes

having a direct impact on the carbon content of rivers and lakes (Hood et al., 2005, Schiff et al., 1997, Tipping et al., 2007), and isotopic analysis of carbon from soil profiles verify the change towards older (decreased ^{14}C) carbon further down the soil profile (Billett et al., 2007, Hope et al., 1997).

The changes in carbon isotopic composition in surface waters could ultimately be due to a combination of these three factors. The amount and type of carbon going into surface waters will be entirely catchment dependent, however catchments with more agricultural usage would undoubtedly witness increasing levels of older carbon.

Links between carbon isotopic character and THM formation however pointed to a potential link between older and isotopically heavier carbon forming an increased number of THM. Research into the DBP formation potential of NOM components has frequently highlighted how the HPO fraction has the potential to form an increased number of THM after chlorination (Brown et al., 2010, Jegatheesan et al., 2008, Serrano and Gallego, 2007). Recent research by Bond et al., (2010) on DBP precursor identification has however found that the second highest precursor for $CHCl_3$ formation was aspartic acid – an anionic HPI component of NOM. The research presented in this chapter proposes a link between composition of NOM from a catchment, but also the impact of biological processes within a reservoir, and if the release of soil carbon stocks continues then this could have a detrimental effect on DBP formation in water treatment. It is worth noting however that this is a small and isolated study, and the theory noted would need to be verified through further analysis.

7.7 Conclusions

The work presented in this chapter focused on the potential of carbon isotopic analysis techniques to characterise NOM in surface waters, and in this chapter in particular, to assess the changes in NOM composition and character through reservoirs. The chapter specifically aimed to answer the following questions;

- Can carbon isotope analysis identify differing characteristics in NOM composition in three contrasting surface waters?
- Can carbon isotopic analysis measure the changes in NOM character and composition from source to water treatment works?
- Can carbon isotopic analysis link NOM character to DBP formation?

Carbon isotope analysis of NOM through surface reservoirs successfully demonstrated differences in organic carbon age and source in surface waters feeding WTW for the first time. Carbon isotope analysis provides a fundamental insight into the age, character and type of organic matter entering surface reservoirs.

Isotopic analysis successfully demonstrated how river NOM samples consisted of younger carbon from C3 plants corroborating with existing carbon isotope investigations of UK riverine carbon. Subsequent reservoir storage at all three sites lead to an isotopically heavier ^{13}C signature and decreased percentage modern carbon ^{14}C signature in raw waters. The most noticeable differences were observed at Site 16 and Site 8, sites which are characterised by poor NOM removal through treatment, attributed to a high HPI NOM content. Subsequent research insinuated three causes for the observed changes in carbon

isotopic signatures; the leaching and transport of older carbon from catchments in low flow events, the preferential utilisation of younger NOM by bacterial, and an increase in the release of carbon through the destabilisation of soil carbon stocks.

Comparisons between carbon isotopes and existing NOM characterisation techniques show existing techniques provided little insight into carbon age or source. Correlations between peak C intensity and ^{13}C signatures and ^{14}C percentage modern carbon were identified; however a larger dataset would be beneficial in cementing any potential relationship. Links between carbon isotopic character and THM formation did suggest a link between increased THM formation and reservoir storage, however further research would be needed to investigate any relationships further due to the limited study size.

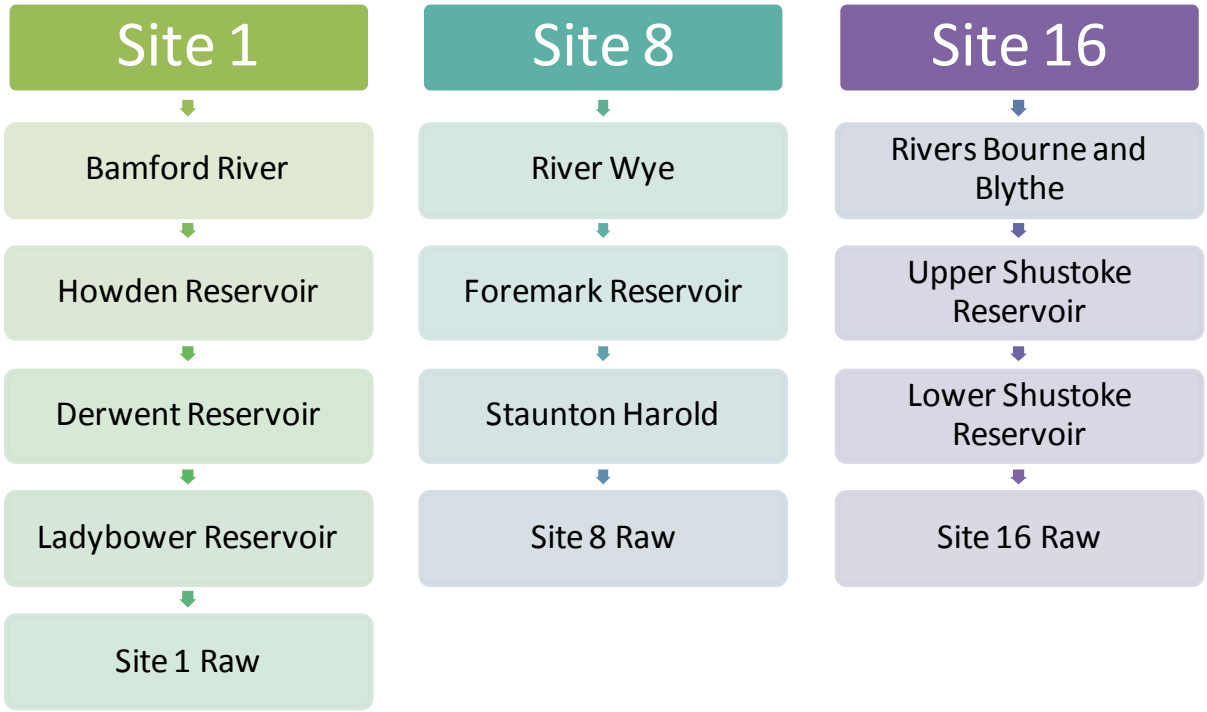


Figure 7.1 – Reservoir flow chart for each site

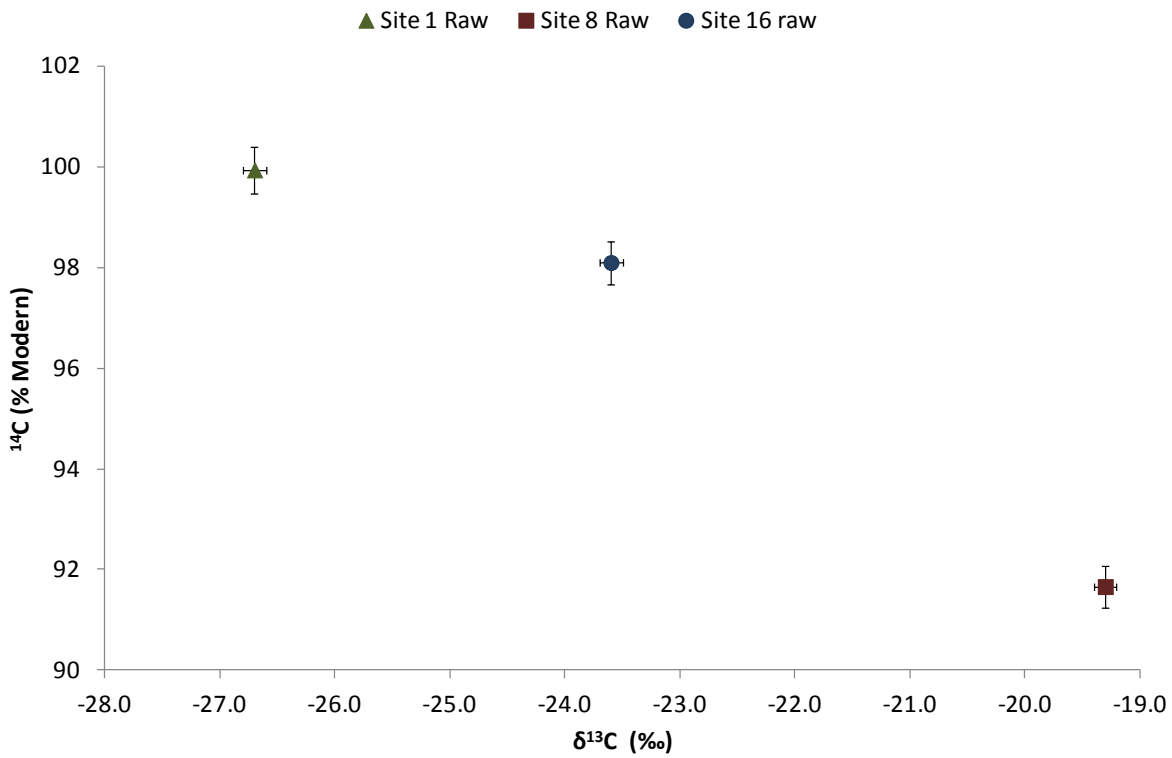


Figure 7.2 – Raw water carbon isotope data

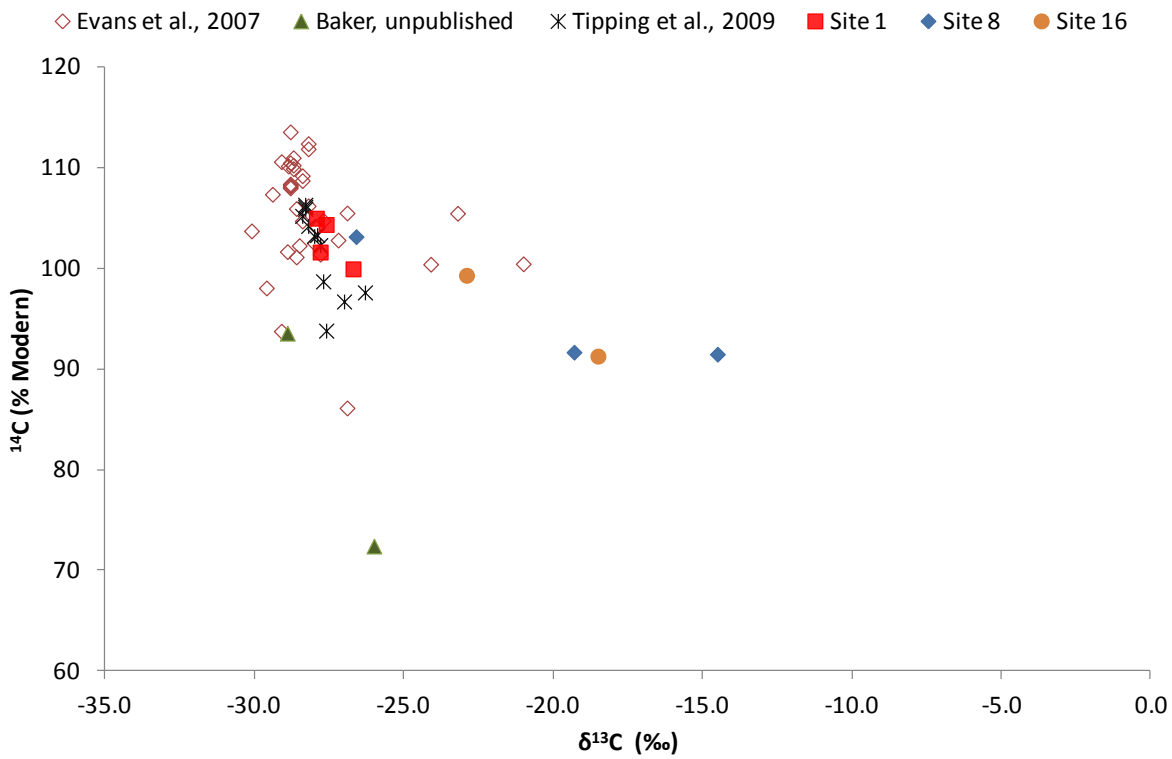


Figure 7.3 – Carbon isotope data for all sites in comparison to published river isotope data

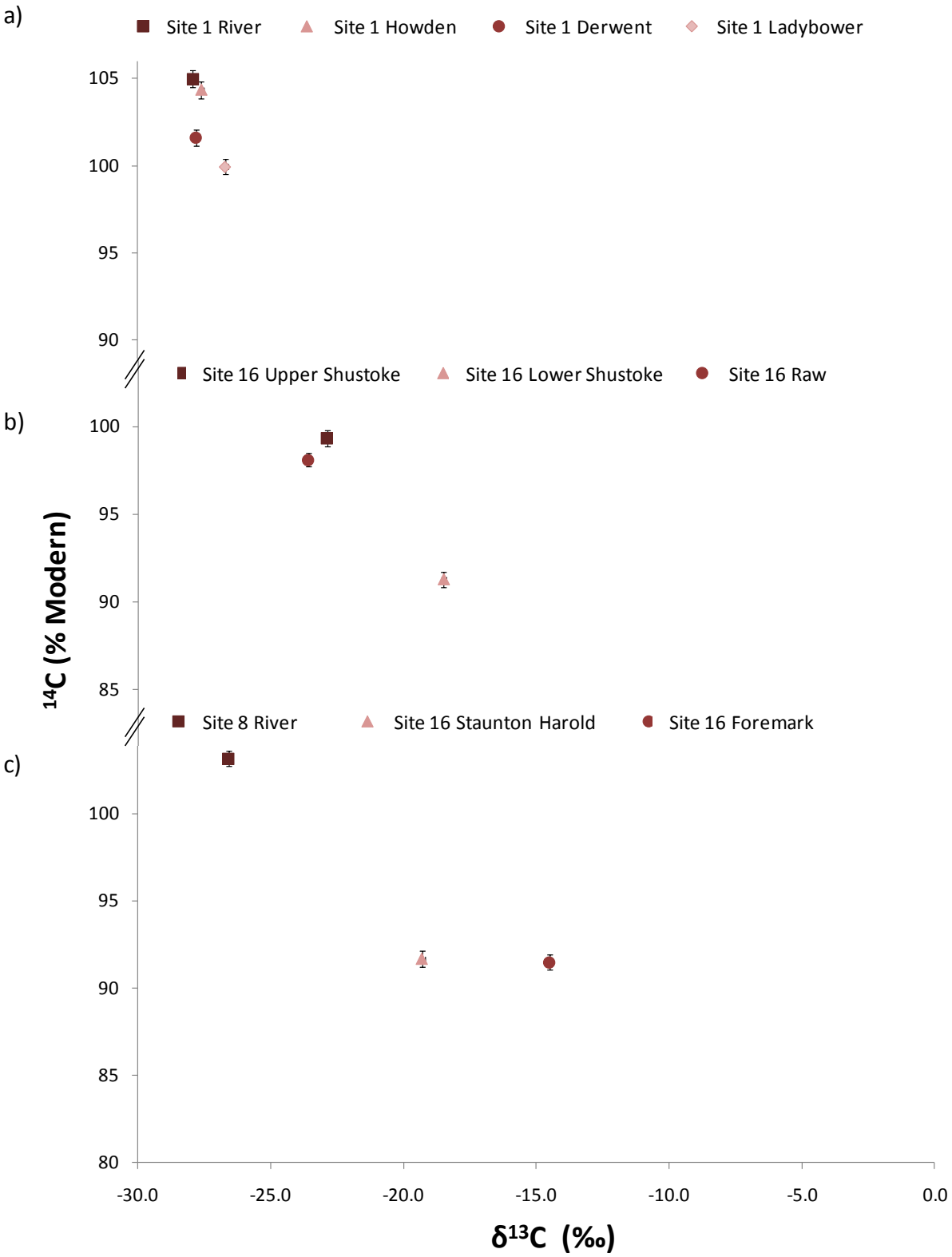


Figure 7.4 – River to WTW carbon isotopes for a) Site 1, b) Site 16 and c) Site 8

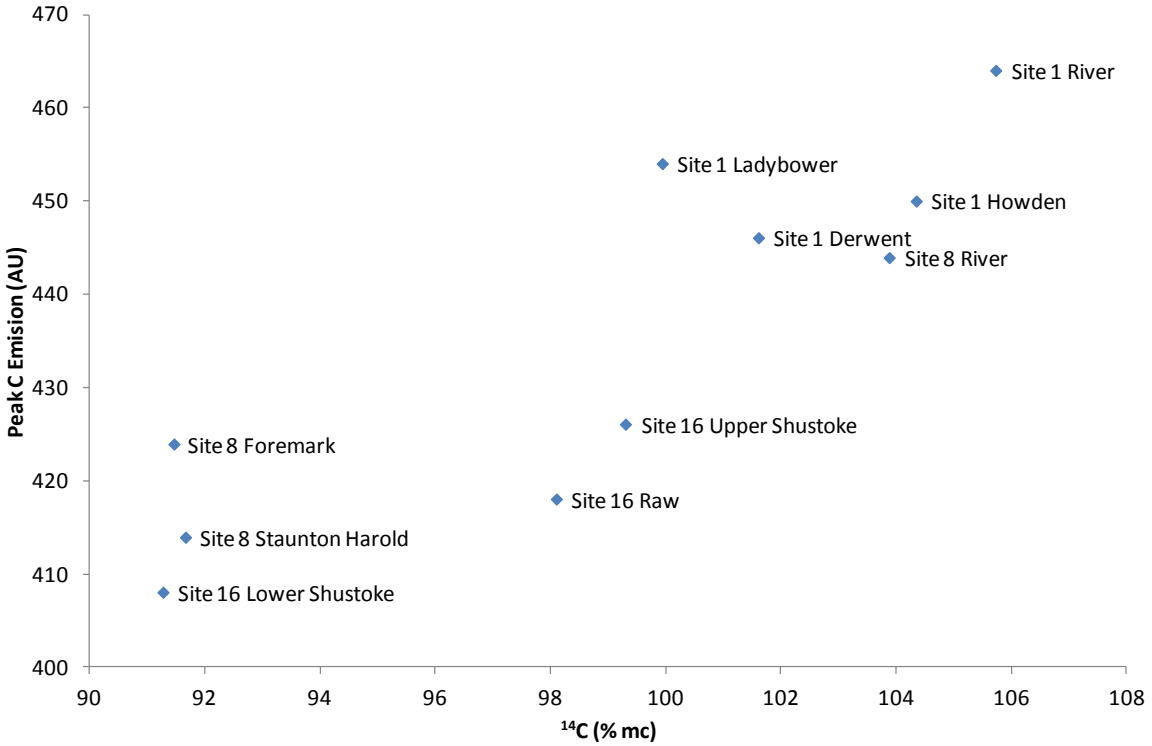


Figure 7.5 – Correlations between ^{14}C and peak C emission

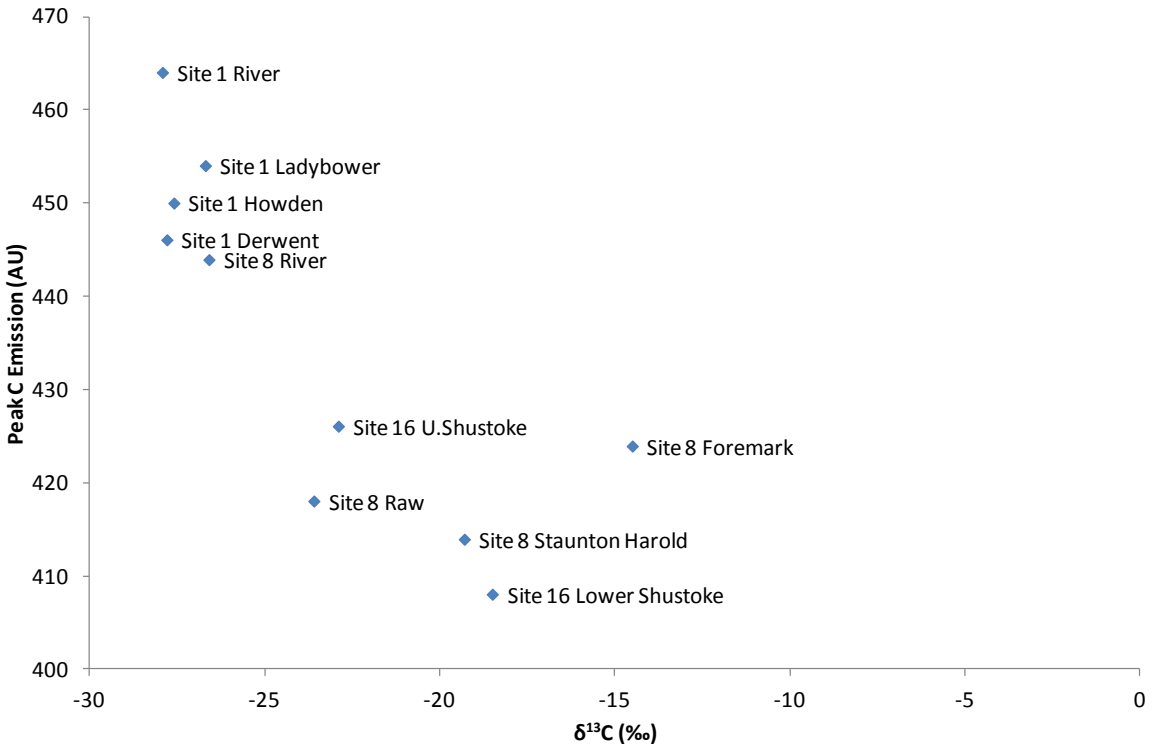


Figure 7.6 – Correlations between ^{13}C and peak C emission

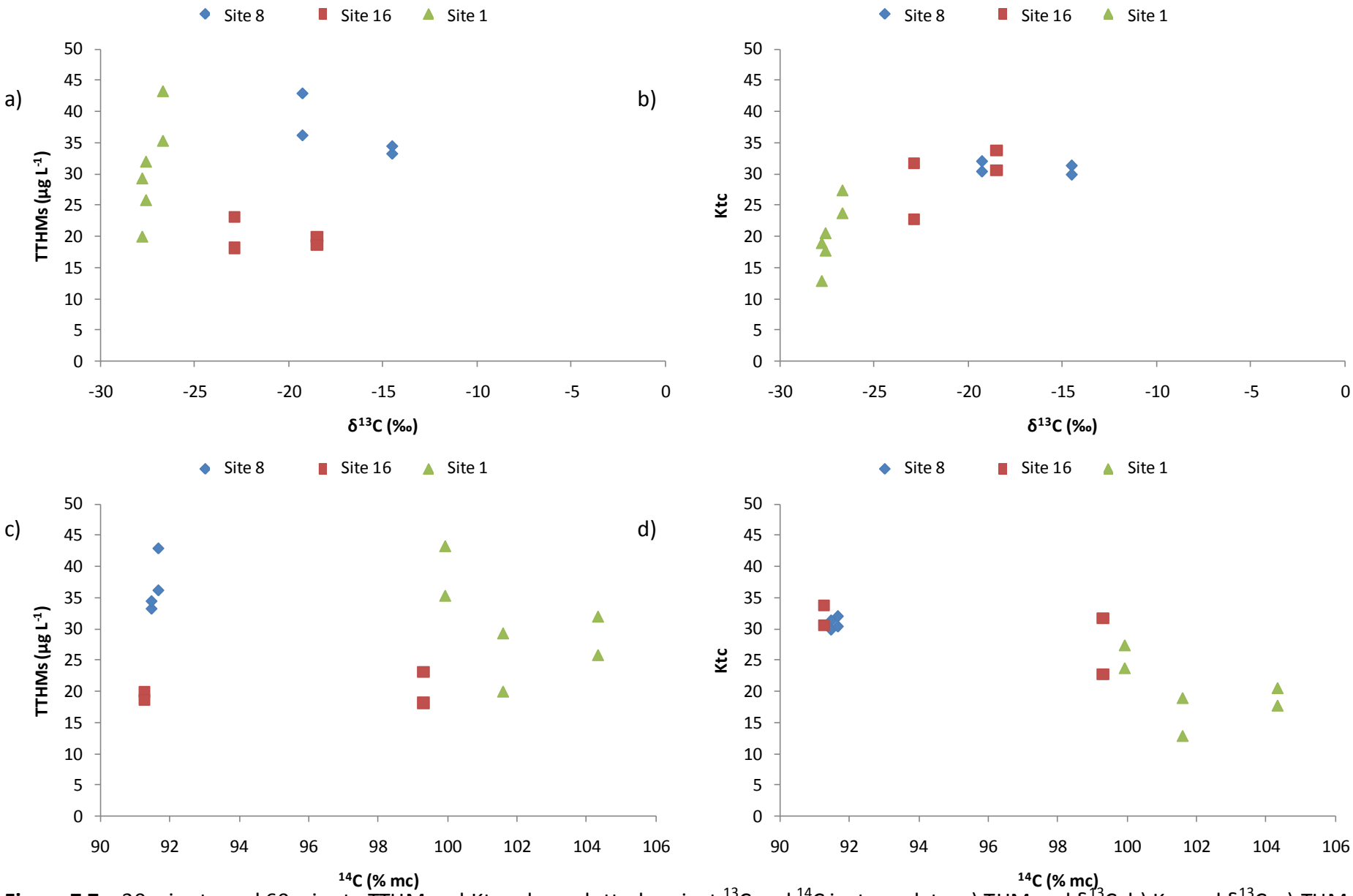


Figure 7.7 – 30 minute and 60 minute TTHM and Ktc values plotted against ^{13}C and ^{14}C isotope data: a) THM and $\delta^{13}C$; b) K_{TC} and $\delta^{13}C$; c) THM and ^{14}C; and d) K_{TC} and ^{14}C

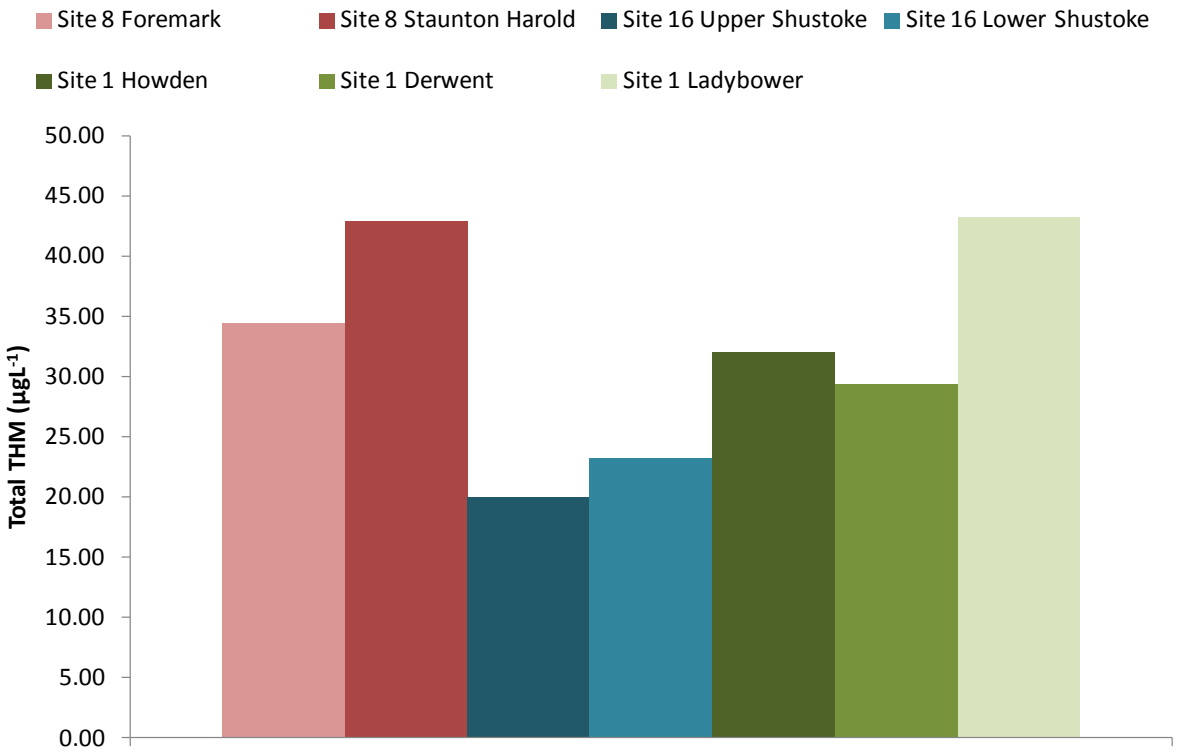


Figure 7.8 – Reservoir THM levels

Chapter 7 Tables

Table 7.1 – Related river carbon isotope investigations

Author	Carbon isotopes	Publication Date
Aitkenhead-Peterson	$\delta^{13}C$ of rural watersheds in south-central Texas (USA)	2009
Amiotte-suchet	$\delta^{13}C$ of DOC in upland forested catchments (France)	2007
Billet	$\delta^{13}C$ and $\Delta^{14}C$ of upland peat catchments (UK)	2007
Butman	^{14}C age ofDOC in freshwater and seawater (USA)	2007
Evans	^{14}C of riverine DOM (UK)	2007
Griffith	$\delta^{13}C$ and ^{14}C age of wastewater treatment plant effluent (USA)	2009
Guo	$\delta^{13}C$ and $\Delta^{14}C$ in the upper Yukon River (Canada)	2006
Helie	$\delta^{13}C$ and $\Delta^{14}C$ in the St Lawrence river (Canada)	2006
Hood	$\delta^{13}C$ and $\Delta^{14}C$ of DOM in a Rocky Mountain stream (USA)	2005
McCallister	$\delta^{13}C$ and $\Delta^{14}C$ of riverine organic matter (USA)	2004
Nagao	$\Delta^{14}C$ of humic substances in Lake Biwa (Japan)	2007
Raymond	$\delta^{13}C$ and ^{14}C %mc of riverine, estuarine and costal DO C (Global)	2001
Schiff	$\delta^{13}C$ and $\Delta^{14}C$ from forested catchments (Canada)	1997
Sickman	$\delta^{13}C$ and $\Delta^{14}C$ of DOC in riverine catchments (USA)	2010
Waldron	$\delta^{13}C$ and ^{14}C %mc of upland rivers with peatland DOC catchments (UK)	2009

Table 7.2 – Sample NOM characteristics

Site	Sample	Turbidity (NTU)	UV_{254} ($abs.m^{-1}$)	DOC ($mg.l^{-1}$)	Peak C Emission (AU)	Peak C Intensity (AU)	Peak T Intensity (AU)
Site 1	Site 1 River	1.7	1.0	7.4	464.0	200.3	116.0
	Howden Reservoir	0.3	0.4	8.0	450.0	144.7	15.2
	Derwent Reservoir	0.6	0.4	4.5	446.1	154.1	16.7
	Ladybower Reservoir	0.6	0.2	9.5	454.0	121.4	15.2
Site 8	River Wye	1.8	0.2	6.2	443.9	216.8	64.9
	Foremark Reservoir	0.8	0.1	3.7	423.9	115.9	39.1
	Staunton Harold Reservoir	0.3	0.1	4.4	413.9	156.5	35.2
Site 16	Upper Shustoke Reservoir	0.7	0.3	9.6	426.1	281.4	61.1
	Lower Shustoke Reservoir	0.3	0.1	5.4	408.0	148.9	38.2
	Site 16 WTW raw	1.4	0.2	7.2	418.0	183.8	69.8

Table 7.3 – Carbon isotope data for all sampling points

Site	Sample	^{14}C (%mc)	Conventional radiocarbon age (years)	$\delta^{13}C$ (‰)	Sample dates
Site 1	**Site 1 River**	104.97 ± 0.46	modern	-27.93	12th August 2009
	Howden Reservoir	103.60 ± 0.48	modern	-27.60	12th August 2009
	Derwent Reservoir	100.89 ± 0.47	modern	-27.80	12th August 2009
	Ladybower Reservoir	99.23 ± 0.46	5 ± 37	-26.70	12th August 2009
Site 8	**River Wye**	103.14 ± 0.49	modern	-26.60	11th August 2009
	Foremark Reservoir	91.46 ± 0.42	717 ± 37	-14.50	11th August 2009
	Staunton Harold Reservoir	91.01 ± 0.42	699 ± 37	-19.30	11th August 2009
Site 16	**Upper Shustoke Reservoir**	98.59 ± 0.46	57 ± 37	-22.90	11th August 2009
	Lower Shustoke Reservoir	90.62 ± 0.40	734 ± 35	-18.50	11th August 2009
	Site 16 WTW raw	98.10 ± 0.43	154 ± 35	-23.60	21st July 2009

Table 7.4 – Typical ^{13}C signatures*

Material	$\delta^{13}C$ Value (per mille)
Wood, peat and many C_3 plants	-30 to -25 ‰
C_4 plants	-9 to -16 ‰
Bone collagen	-19 ‰
Freshwater plants	-16 ‰
Arid zone grasses	-13 ‰
Marine organic carbon**	-18 to -22 ‰
Maize	-10 ‰
Atmospheric CO_2	-8 ‰
Marine carbonates	0 ‰

*Adapted from (Bowman, 1990)

**(Bauer, 2002)

Table 7.5 – R^2 Correlations with NOM characterisation data

	^{13}C	^{14}C
UV_{254}	0.35	0.48
SUVA	0.44	0.52
Peak C Emission	0.65	0.75
Peak C Intensity	0.06	0.13
Peak T Intensity	0.01	0.09
TOC	0.16	0.13
Turbidity (NTU)	0.12	0.30

Chapter 8. Carbon isotopic analysis through the water treatment process

8.1 Introduction

In July and October 2008, a preliminary investigation of post-GAC waters from six surface water sites in the Midlands area of the UK was conducted. This investigation focused on investigating a relationship between post-GAC waters and THM precursors. Results from the investigation showed significantly different radiocarbon isotope values than those typically reported for NOM in UK river waters (table 8.1). These results are discussed in more detail in section 8.2, however both July and October 2008, Post-GAC NOM shifted towards isotopically heavy ^{13}C and depleted percentage modern ^{14}C in post-GAC waters, suggesting an input of carbon at a stage in the treatment process. A subsequent investigation was then proposed to concentrate on two WTW in the Severn Trent area in order to identify an input of carbon during treatment.

This chapter aims to investigate the impact of water treatment on carbon isotope signature and consider explanations for the isotopically heavy ^{13}C and depleted percentage modern ^{14}C found in post-GAC waters.

The work in this chapter focuses on addressing objective (ii):

To investigate the potential for carbon isotopic analysis and environmental colloidal analysis as NOM characterisation tools, to address current characterisation needs and to identify trends with DBP formation.

In particular, this chapter focuses on the following questions;

- Does water treatment adversely affect the carbon isotope signature of DOC?
- What are the possible causes for variations in carbon isotope signatures?
- Can carbon isotopic analysis of DOC provide reliable and robust information on DOC composition and character through the water treatment process, compared with existing methods?

These objectives were investigated by sampling intake, post-clarification, post-filtration, post-GAC and disinfected waters were collected from Site 8 and Site 16 WTW in June 2009, in addition to the 2008 post-GAC samples. Samples were filtered through 0.7 µm glass microfiber filters (as is standard with carbon isotopic analysis), with two unfiltered post-GAC and disinfection samples also collected. NOM characterisation was performed using UV_{254} and fluorescence, with NTU, DOC and THM analysis also obtained.

8.2 Initial investigations into post-GAC carbon isotopes

$\delta^{13}C_{(VPDB)}$‰ and ^{14}C (%mc) values from post-GAC waters collected from reservoir water at six WTW are shown in figure 8.1 to highlight differences which may potentially be attributed to seasonal and/or catchment influences. In comparison to 2009 data from Site 16 and Site 8, 2008 post-GAC (P-GAC) samples show greater variations in the percentage modern carbon

^{14}C, and all sites exhibit an isotopically heavier $\delta^{13}C$, suggesting that at the time of sampling 2008 P-GAC NOM samples are derived from vastly different source materials. P-GAC waters at Site 5 have the highest percentage modern carbon ^{14}C signatures at 102.04 and 102.67 %mc for July and November waters respectively (table 8.1). As they are above 100 %mc, this shows ^{14}C signatures are modern and the average age of DOC is between zero and fifty years old. Site 3 has the lowest percentage modern ^{14}C signatures at 80.26 and 88.00 %mc in July and November respectively, indicating the ^{14}C signature of the source DOC at Site 3 is much older than that of DOC at Site 5. As previously discussed in chapter 7, this could be due to differing land use patterns within the catchment, releasing older carbon into surface waters.

Site 13 and Site 3 are the only two sites to see large changes in ^{14}C signatures between sampling periods. Both sites display increases in ^{14}C from July to November, indicating an increase of younger organic material. This could be attributed to seasonal effects, with autumn flushes transporting younger organic material to surface waters from the catchment. $\delta^{13}C$ at Site 2 and Site 5 show a shift towards an isotopically heavier $\delta^{13}C$ signature in November samples. In contrast, November samples at Site 13 and Site 3 shift towards an isotopically lighter $\delta^{13}C$ signature within the same period. These shifts could be seasonally influenced or in response to changes in filtration and GAC media. With $\delta^{13}C$ signatures ranging from -18.12 ‰ at Site 13 to -7.86 ‰ at Site 3, further investigation is still needed to attribute a significantly heavier $\delta^{13}C$ signature than is typically seen in UK surface waters.

Comparisons between surface water DOC collected by Evans et al. (2007), Baker, (unpublished), Tipping et al. (unpublished), Chapter 7 reservoir data and WTW isotope data shown in figure 8.2 demonstrates a shift towards an isotopically heavier $\delta^{13}C$ signature and decreased ^{14}C percentage modern values in 2008 post-GAC samples at all six surface water sites. An isotopically heavier $\delta^{13}C$ could indicate an input of DOC from another source (i.e. older carbon), or that the carbon has gone through a fractionation process where ^{12}C has been released during a chemical reaction, leaving a decreased $\delta^{13}C$. The decreased percentage modern ^{14}C indicates that samples are of a much older carbon signature compared to the younger carbon signatures shown in raw stream water data. Reservoir data displayed in Chapter 7 for sites Site 1, Site 16 and Site 8 range between expected values from published river data to 2008 P-GAC data. At Site 1, $\delta^{13}C$ values stay within a 2σ confidence limit, and the only evidence of changing NOM is at decreasing ^{14}C percentage modern from river to the furthermost reservoir, Ladybower. In the more lowland sites, Site 8 and Site 16 ^{13}C results shift towards an isotopically heavier $\delta^{13}C$ with increasing time in reservoir storage.

8.3 Carbon isotope analysis through a water treatment works

The unexpected results of post-GAC carbon isotopic samples from the 2008 study prompted concerns over the impact of water treatment on organic matter, and specifically carbon isotope signatures. It was therefore logical to conduct further analysis into the fate of carbon isotopes though the treatment process to assess any impacts on carbon isotope signatures of water treatment and to investigate the possibility of carbon addition. The various processes at WTW remove OM in different ways; for example coagulation and

clarification remove OM through destabilisation and precipitation mechanisms (Duan and Gregory, 2003), whereas GAC is an adsorption process (Bond et al., 2011). It would therefore be prudent to assess the impact of the various treatment methods on carbon isotopes. However, treatment at Severn Trent WTW all have very similar processes, with any variations usually focussed on clarification. Variations in the 2008 samples would therefore be impacted predominantly by the changing character of OM in raw waters.

Site 8 and Site 16 were chosen as the two sites for further investigation as they were both in the original six sites and they had the two most contrasting catchments and raw surface water characteristics. Site 8 waters characteristically contain a seasonally variant mixture of molecular weights, and HPI and HPO NOM. Due to an average HPI content of 45% in source water, conventional coagulation with alum or ferric is limited. However, DOC removal of up to 70% can still be achieved with optimised processes. The catchment land use is predominantly arable and pastures (43% and 30% respectively), with a small urban area indicating a dominance of HPO humic and fulvic NOM. This is verified by a high SUVA content of 4.85 L mg^{-1} m^{-1} in raw waters as shown in table 8.2.

Site 16 is a typically lowland catchment, exhibiting high quantities of HPI material in raw source waters demonstrated by a low SUVA of 2.75 L mg^{-1} m^{-1} (table 8.2). Again, a dominance of HPI material reduces conventional treatment effectiveness, therefore DOC removal is generally below 25%. Catchment usage at Site 16 indicates a distinct contrast with the Site 8 catchment with a higher percentage of arable land use and up to 32% for industrial, transport or commercial usage (Bieroza et al., 2009b). Although Site 16 has a

higher initial DOC content, a lower SUVA value indicates a dominance of the more difficult to remove HPI NOM.

Samples for Site 8 and Site 16 were taken in June 2009. From trends reported in scientific literature and the fractionation data from earlier studies in the thesis, the general composition of NOM at both sites would be likely to have a higher percentage of HPI material when sampled (Scott et al., 2001, Sharp et al., 2006e). This would impact on the observed DOC removal seen at both WTW as HPI NOM is more difficult to remove through conventional treatment. THM levels are reported to be higher in the summer months due the effect of temperature on formation potential (Goslan et al., 2002, Serrano and Gallego, 2007), so THM levels recorded from the two sites would be directly impacted by this.

Raw water samples for both Site 8 and Site 16 have an isotopically heavier $\delta^{13}C$ signature than initial treated samples (post-clarification) but lie within the range of typical UK values. Data sourced through the water treatment process and shown in table 8.2 demonstrate that $\delta^{13}C$ values for DOC get lighter with each treatment stage, and colloidal signatures are heavier than raw waters. Each of these can be considered on a site-by-site basis as the carbon isotopic signature of both dissolved and colloidal NOM is determined at different treatment stages.

Comparisons between radiocarbon isotopes at each stage of water treatment are shown in figure 8.3 and table 8.2. At Site 8, ^{14}C (%mc) values show that raw waters are oldest and increase in ^{14}C activity (%mc) after clarification. This indicates that coagulation and flocculation treatment processes, well noted for targeting more readily removed larger

NOM with higher charge densities, target the older NOM fraction likely to be the humic and fulvic acids of HPO NOM. Apart from raw and colloidal fractions, ^{14}C values are all within 3 %mc which further substantiates this theory. Post-GAC, dissolved (<0.7 µm) NOM ^{14}C increases, whilst colloidal NOM ^{14}C decreases (0.7-2 µm) indicating there is older carbon in this fraction or an addition of GAC fines. SUVA calculations on the dissolved fraction imply HPI is increasingly dominant through treatment: we hypothesise that colloidal material is likely to contain any remaining untreated HPO NOM. $\delta^{13}C$ signatures for dissolved NOM remain in the range attributed to C3 plants, however the colloidal fraction is shown to contain a source of additional carbon in the 0.7 to 2 µm size range with an average $\delta^{13}C$ value of -15.80‰. The source of this is uncertain but one possibility is that colloidal NOM has undergone chemical fractionation of $^{12}C/^{13}C$ during the coagulation/aggregation processes as ^{12}C is more labile and lighter than the heavier $\delta^{13}C$. Treatment processes could cause chemical fractionation, and as ^{12}C is more likely to react it will require less energy to break the chemical bond between the ^{12}C and another atom. If this fractionation culminates in the formation of CO_2, CO_2 degassed from the water will preferentially contain the lighter ^{12}C isotope, leaving the remaining NOM enriched with the heavier $\delta^{13}C$.

At Site 16, ^{14}C (%mc) values are less variant compared to Site 8, and most likely due to the targeted removal of specific NOM fractions in each treatment process rather than an additional carbon source. In contrast with Site 8, ^{14}C values for filtered and unfiltered GAC and final water samples are within 1σ confidence limits indicating that colloidal NOM at Site 16 consists of younger organic carbon than at Site 8. GAC processes at Site 16 removes the largest amount of DOC during treatment (table 8.2) which could attribute to an increase in ^{14}C (%mc) values if larger, peat derived humic acid fulvic acids remain. A limited decrease in

^{14}C values from post-GAC to final waters is imaginably attributable to NOM reacting with chlorine at the disinfection stage (Roccaro et al., 2008). All samples are within one sigma confidence limits for ^{14}C (%mc), therefore notable distinctions can only be made on $\delta^{13}C$ values.

Site 16 shows noticeable separation of $\delta^{13}C$ values between filtered and unfiltered post-GAC and final samples (-29.1 to -22.9 ‰ and -26.9 to -22.9‰ respectively). Whilst this is not as exaggerated as differences found at Site 8 it adds further to evidence of an additional carbon source being added to the colloidal fraction post-GAC.

At both sites there are shifts towards decreased percentage modern ^{14}C signatures in final water carbon isotope signatures compared to P-GAC data. At both sites, final water samples were taken after the addition of chlorine disinfectants. After a small contact time, it is evident that the addition of chlorine decreases the percentage modern ^{14}C from 97.27 to 95.11 %mc at Site 8 (filtered samples) and 97.14 to 96.27 %mc at Site 16 (filtered samples) through targeting the younger NOM which was not removed in the previous treatment processes. A shift towards a decreased percentage modern ^{14}C signature in unfiltered samples is also observed in colloidal fractions at Site 16, however in contrast, Site 8 colloidal fractions increased after disinfection.

In comparison to the 2008 P-GAC data, samples from Site 16 in 2009 have an increased percentage modern carbon ^{14}C and isotopically lighter $\delta^{13}C$. A similar pattern is evident with Site 8 waters, suggesting that if colloidal material had a decreased percentage modern ^{14}C signature, it could potentially have an isotopically heavier $\delta^{13}C$ signature.

Existing NOM characterisation methods such as UV, turbidity, TOC and fluorescence are typically used to give an insight into changes in NOM composition and character through the treatment processes. Concentrations of NOM in samples are usually measured using TOC and UV_{254}. UV_{254} measurements also demonstrate NOM aromaticity but are limited to the amount of activated chromophores visible at any specific wavelength. TOC and UV_{254} measurements through both sites treatment processes display the removal of NOM, most prominently after clarification and GAC. TOC measurements indicate an overall higher level of NOM removal at Site 16 than Site 8. UV_{254} measurements also verify this, however overall TOC at Site 16 is higher than Site 8, indicating a dominant HPI fraction in final waters. SUVA measurements for both waters demonstrate the targeted removal of NOM fractions through each treatment stage. For example, at Site 8, post-clarification SUVA decreases from 4.85 to 3.71 L mg^{-1} m^{-1}, suggesting the larger HPO NOM has been predominantly removed. This then increases to 3.18 L mg^{-1} m^{-1} post-clarification and then again in post-GAC samples, suggesting final are dominated by HPI NOM. A similar trend is visible at Site 16 WTW, however a decrease in UV_{254} in final waters suggests an additional removal after GAC which could be attributed to NOM settling or, most likely, reactions between chlorine disinfectants and remaining NOM. The use of SUVA for organic characterisation is a widely deliberated topic in recent scientific literature however. SUVA is widely used in many NOM characterisation studies (Ates et al., 2007a, Chow et al., 2008a), and subsequent relationships with the characterisation of DBP precursors (Fabris et al., 2008), however there are a number of studies that found no link to DBP formation or precursors and challenge the use of SUVA as a characterisation tool due to its limitations in identifying charge-less HPI material (Parsons, at al., 2004, Weishaar et al. 2003). In this study however

SUVA measurements were used to illustrate the changing character of NOM through water treatment processes, and used in conjunction with other NOM characterisation methods.

Due to the sample preparation techniques of UV_{254} and TOC, and the treatment processes themselves, little variation is evident between colloidal and dissolved fractions. Fluorescence spectroscopy measurements for peaks C and T (table 8.3) show small variations between dissolved and colloidal fractions, but further statistical analysis shows very little difference between size fractions. Figure 8.4 demonstrates the strong link between peak C intensity and DOC for both sites, demonstrating fluorescence is potentially best applied in the identification of total DOC in samples and aromaticity content. Statistical analysis for links between existing NOM characterisation methods and carbon isotopes proved unsuccessful, thus promoting the use of carbon isotopes for additional characterisation analysis.

8.4 Possible explanations for isotope variations

Results showing shifts towards isotopically heavier $\delta^{13}C$ could be attributable to three possible scenarios. These are:

- Fractionation of $\delta^{13}C$ during treatment;
- An inorganic/organic carbon interaction;
- An input of dissolved carbon during the treatment process.

Chemical fractionation of $^{12}C/^{13}C$ during the coagulation/aggregation processes, as previously discussed in section 8.3 occurs when a bond containing an atom or its isotope is

broken during a (bio)chemical processes which is ultimately influenced by the bond strength and bond length. Differences in vibration energy levels of bonds involving heavier isotopes as compared to lighter isotopes mean less energy is needed to break bonds between lighter isotopes (Meier-Augenstein, 2010). ^{12}C is a lighter isotope than ^{13}C, so ^{12}C bonds will be preferentially broken, carbon is oxidised to CO_2, leaving an isotopically heavier $\delta^{13}C$. Chemical fractionation by means of a kinetic effect where a chemical bond is broken or formed in the rate-determining step of the reaction or by changes in physiochemical properties will almost certainly occur at some stage within water treatment due to the nature of the treatment processes in use (Rieley, 1994). $\delta^{13}C$ values are presented in per mille, so fractional difference between ^{13}C and ^{12}C is displayed in parts per thousand. Any chemical fractionation would only result in very small differences between the amounts of ^{12}C and ^{13}C and would be unlikely to be attributable to the large shifts towards isotopically heavier $\delta^{13}C$ seen at the sites (Meier-Augenstein, 2010). Figure 8.5 demonstrates the ranges of soil-derived CO_2 for C3 and C4 plants, and whilst fractionation of SOM does cause a heavier $\delta^{13}C$, values remain within one sigma confidence limit (Werth and Kuzyakov, 2010). This demonstrates that for C3 plants, fractionation of SOM during coagulation would have little effect on the overall $\delta^{13}C$ signature, and is therefore unlikely to cause the observed shifts in post-GAC samples.

Contribution of inorganic carbon (IC) to freshwater IC pools by bedrock, atmospheric carbon and respired CO_2 organic carbon by chemical and biological processes can result in isotopically heavier $\delta^{13}C$ signatures. Biologically assimilated IC from bedrock could also dramatically decrease the percentage modern of ^{14}C. Catchments have little or no source of inorganic carbon, and the only source of inorganic carbon from within the treatment

process could be concrete, used in WTW construction. As water is in one specific area for no longer than 40 minutes at a time and in the treatment process for approximately three hours, it is unlikely that inorganic carbon could adsorb onto the organic matter. At WTW where a lower coagulation pH is used, there is evidence of the degradation of concrete structures, however at both Site 16 and Site 8, coagulation pH is approximately 7.2, which would not cause the degradation of the concrete structures. This scenario is most unlikely however as when samples are sent for carbon isotopic analysis, inorganic carbon is removed from the samples via the process of nitrogen sparging. Samples are acidified to pH 4, which moves the bicarbonate equilibrium in favour of CO_2 formation (eqn in methods and materials), followed by nitrogen sparging to remove dissolved CO_2 from the sample. Extreme care is then taken to prevent any additional carbon (organic or inorganic) from contaminating the sample during the subsequent treatment processes before graphitisation (see relevant methods and materials section).

A third possible explanation is an input from some stage in the treatment process. Ferripol XL ($FeSO_4$) is a coagulant added at these sites to reduce repulsion forces between particles, thus promoting particle bonds and the formation of flocs, removing material out of suspension and is marketed as containing no carbon. A known quantity of Ferripol XL was combusted with known age ^{14}C standards TIRI Barleymash and Heidelberg Wood (Scott, 2003). Results were not stastically different from published values which shows no addition of carbon from the Ferripol XL. This makes the variation in carbon isotope signatures in treated water samples from an input of Ferripol XL improbable. During the treatment process, water passes through filtration media and GAC media to remove impurities in the water. Table 8.4 shows the carbon isotope signatures for the filtration and GAC media from

Site 8 and Site 16. Filtration media for both sites ranges from 0.07 to 3.73 %mc ^{14}C (figure 8.6). Any overlap in the ^{14}C signatures is most likely due to the construction of a filter bed, such that filter media is layered in the vessel so some crossover between media could occur.

GAC media ^{14}C is again composed of much older material, apart from the coconut trial media found at Site 16 which is composed of 98.61 %mc. At Site 16, coconut trial material is in a separate GAC vessel and water passing through is not additionally passed through a carbon vessel. All but the recently regenerated (two weeks) GAC media at Site 16 show an increase in ^{14}C percentage modern the longer the media is in use. This could be a sign of adsorption of DOC onto the GAC media or microbial growth on the column. $\delta^{13}C$ signatures for both Site 8 and Site 16 GAC media range from -22.7 to -23.9 ‰, which is in the same region as Site 16 colloidal $\delta^{13}C$. These results strengthen the theories that there is a carryover of GAC fines in the colloidal fraction and microbial growth which could alter the carbon isotope signatures for NOM in the colloidal size range.

8.5 Discussion

The use of carbon isotopic analysis for characterisation of surface water DOC has mainly been used in studies to assess the impact of land use management and investigating the transport of carbon through surface waters (Austnes et al., 2010, Guo and Macdonald, 2006, Hood et al., 2005). Recent research has also used carbon isotopic analysis to illustrate the rise of DOC in source waters in Northern Europe and America (Evans et al., 2007, Sickman et al., 2010) and for the use of characterisation of organic matter in surface waters (Esteves et al., 2007, McCallister et al., 2004, Megens et al., 2002). Due to the outcomes of this

research and the information obtainable on carbon character in surface waters, it was deemed carbon isotopic analysis could provide an additional insight into the character of NOM in surface waters that conventional characterisation methods would not be able to offer.

Initial use of carbon isotopic analysis of surface waters at three sites, depicted in chapter 7 showed carbon isotopic analysis was able to successfully distinguish between sites, and also illustrate the impact reservoir storage has on DOC. It was then logical to continue analysis of DOC using carbon isotopes to assess the impact of water treatment processes. Initial comparisons between the two sites clarified the dissimilarity between catchment characteristics. ^{14}C values of results demonstrated raw water Site 8 consisted of NOM with an older carbon source than Site 16, indicative of humic and fulvic material in soils being the main source for NOM to this WTW (see chapter 3, table 3.2).

Through the water treatment process however, results for both sites showed a shift towards an isotopically heavier $\delta^{13}C$ signature in the colloidal fraction and a decreased percentage modern carbon ^{14}C after various stages. A decreased ^{14}C percentage modern carbon after clarification and filtration indicated that the treatment processes are targeting the older NOM fraction, likely to be the humic and fulvic acids of HPO NOM present in soils. Whilst both sites experienced small changes in the isotopic composition of carbon through the WTW, a decrease in percentage modern ^{14}C post GAC in the colloidal fraction at Site 8 was observed.

Literature regarding the occurrence of older carbon (decreased ^{14}C) in surface waters indicates how changing land use patterns are mobilising carbon pools from soil stocks, increasing overall levels of DOC in surface waters, and also the release of older carbon (Tipping et al., 2010, Evans et al., 2006). Recent literature on surface water $\delta^{13}C$ has not reported variations such as those recorded in post-GAC colloidal analysis however.

Colloidal fractions at both sites contain NOM with an isotopically heavier $\delta^{13}C$. A review of current literature on the variations in ^{13}C suggested three potential scenarios for the observed trends; fractionation of $\delta^{13}C$ during treatment; an inorganic/organic carbon interaction; and finally an input of dissolved carbon during the treatment process.

Fractionation of $^{12}C/^{13}C$ through treatment (chemical or biological) could feature in an explanation for the occurrence of a heavier $\delta^{13}C$ signature as the isotopically lighter ^{12}C requires less energy to break chemical bonds, escaping as gaseous CO_2 leaving the heavier ^{13}C, but could not be accountable for a large shifts in the $\delta^{13}C$ signature (Werth and Kuzyakov, 2010). An inorganic carbon interaction would have to come from within the treatment works, as both catchments have little or no source of dissolved inorganic carbon (DIC) (e.g. bedrock or significant urban land cover) so it is unlikely that the NOM isotopic signature is derived from DIC incorporated into the catchment NOM pool via photosynthesis. Finally, an input of organic carbon from within the treatment process could only come from GAC, as carbon isotopic analysis of iron coagulant was not dissimilar to organic carbon results. An addition of GAC fines has previously been reported in scientific literature (Vuorio et al., 1998), with also GAC breakthrough having a significant impact on treatment performance (Babi et al., 2007, Philippe et al., 2010). A review of all three

scenarios indicates that only an addition of GAC fines would be able to account for the observed variation in colloidal ^{13}Csignatures.

8.6 Conclusions

The research presented in this chapter aimed to build on previous investigations into the use of carbon isotopic analysis of surface waters, and investigate the impact of water treatment on isotopic fractions. In particular, the chapter focused on the following questions;

- Does water treatment adversely affect the carbon isotope signature of DOC?
- What are the possible causes for variations in carbon isotope signatures?
- Can carbon isotopic analysis of DOC provide reliable and robust information on DOC composition and character through the water treatment process, compared with existing methods?

Carbon isotope analysis of NOM through water treatment works indicated the age of treated NOM for the first time. Comparisons were made between initial samples collected in 2008 of P-GAC waters from six WTW and published carbon isotope riverine UK data. Results indicate that P-GAC data has an isotopically heavier ^{13}C signature and decreased ^{14}C percentage modern carbon. Further comparison with Chapter 7 riverine and reservoir confirm a predominantly modern carbon isotopic NOM source entering storage reservoirs, although sites Site 8 and Site 16 experience shifts towards a heavier δ^{13}C through subsequent reservoir systems although values are not as extreme as those experienced in 2008 P-GAC samples. Using relevant research on carbon isotopes, three potential

explanations were proposed for the heavier isotope 13 signatures; fractionation of the 12 and 13 carbon isotopes; an inorganic/organic carbon interaction, and an input of carbon from the water treatment process. A review of each scenario indicated that the most plausible explanation lied with an input of carbon from GAC processes.

This therefore leads to the assumption that whilst drinking water treatment is removing DOC, its character is changing through treatment which could be due to an introduction of GAC fines or microbial growth on the GAC column.

The use of carbon isotopic analysis for NOM characterisation has therefore provided an additional, previously unknown perspective into the variations in NOM character between source waters and through the water treatment process that existing methods would be unable to identify.

Chapter 8 Figures

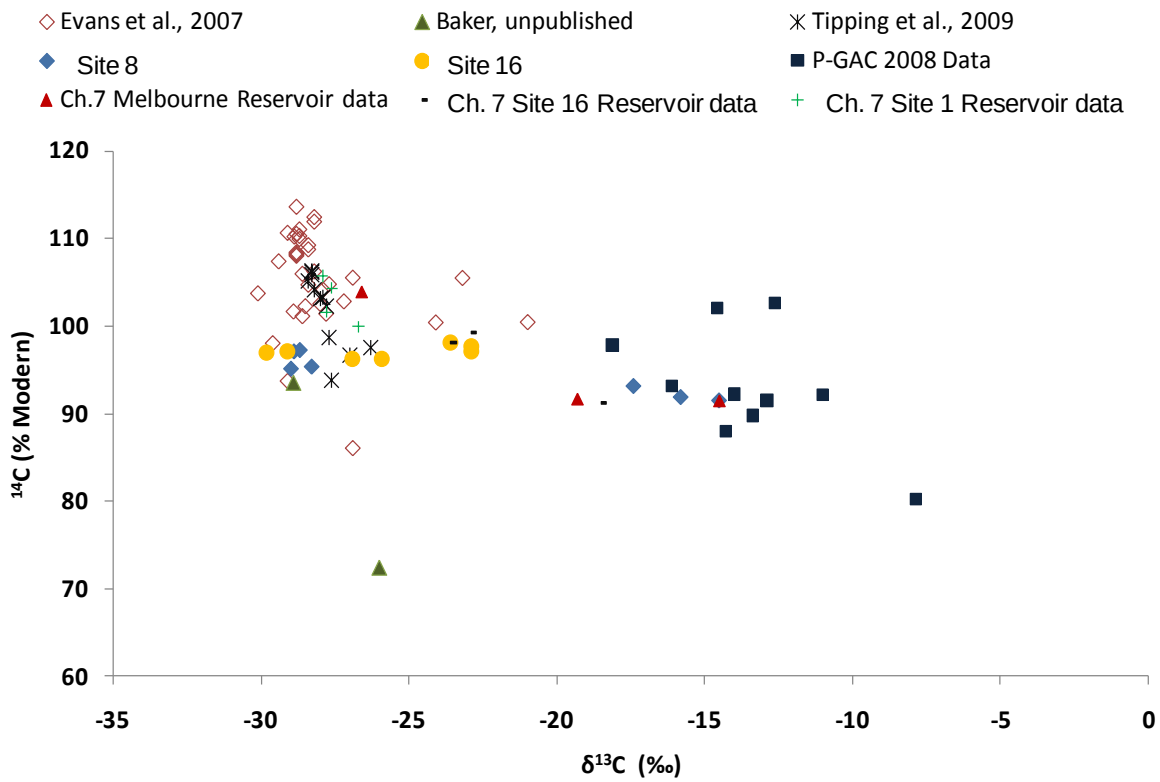


Figure 8.1 – 2008 Post-GAC data

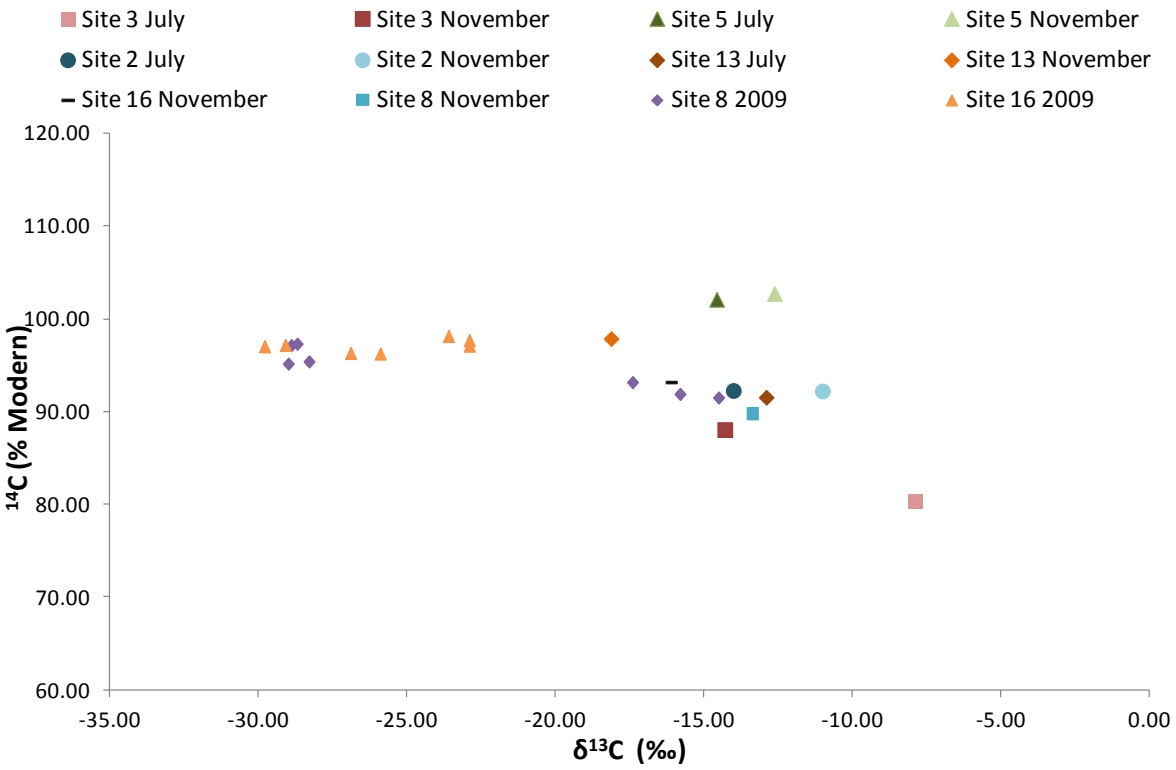


Figure 8.2 – 2008 carbon isotope data for surface waters in comparison with published data

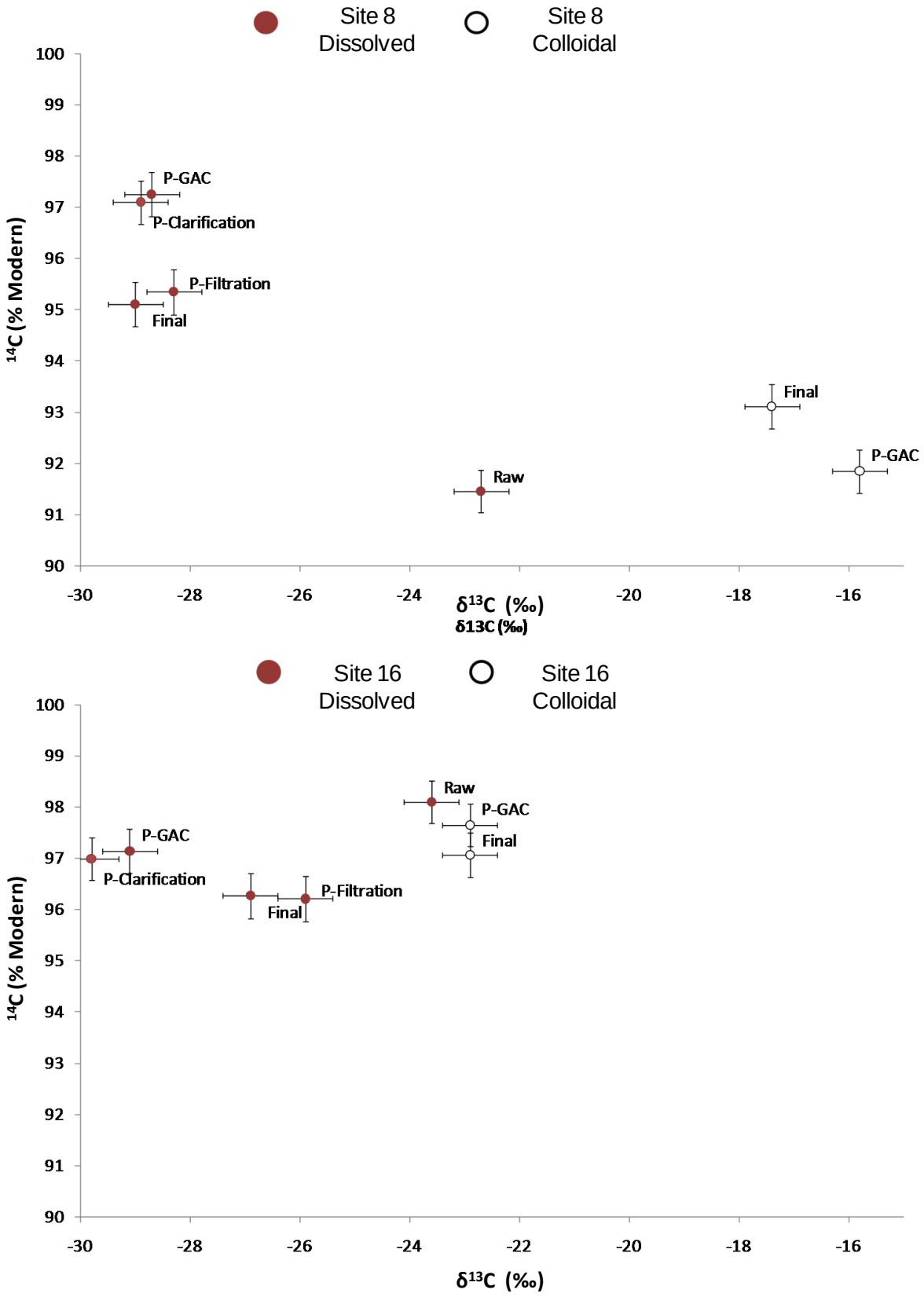


Figure 8.3 – Carbon isotopes through drinking water treatment for Sites 1 and 2

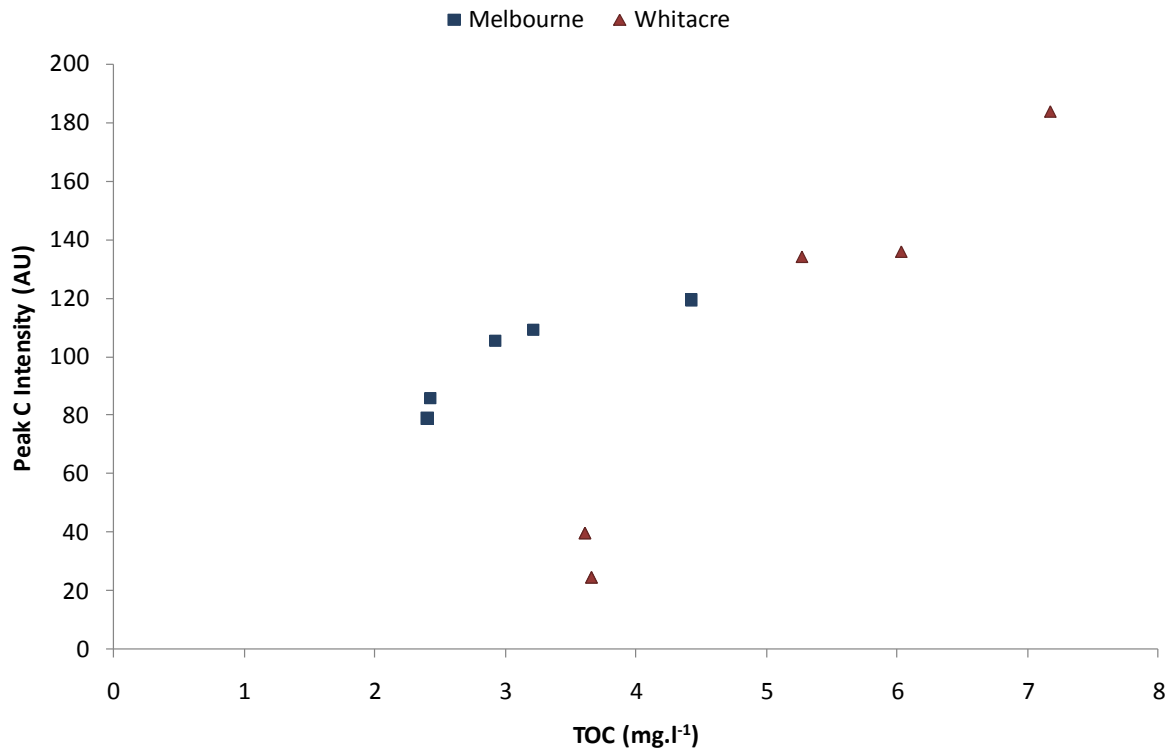


Figure 8.4 – Fluorescence peak C intensity plotted against DOC

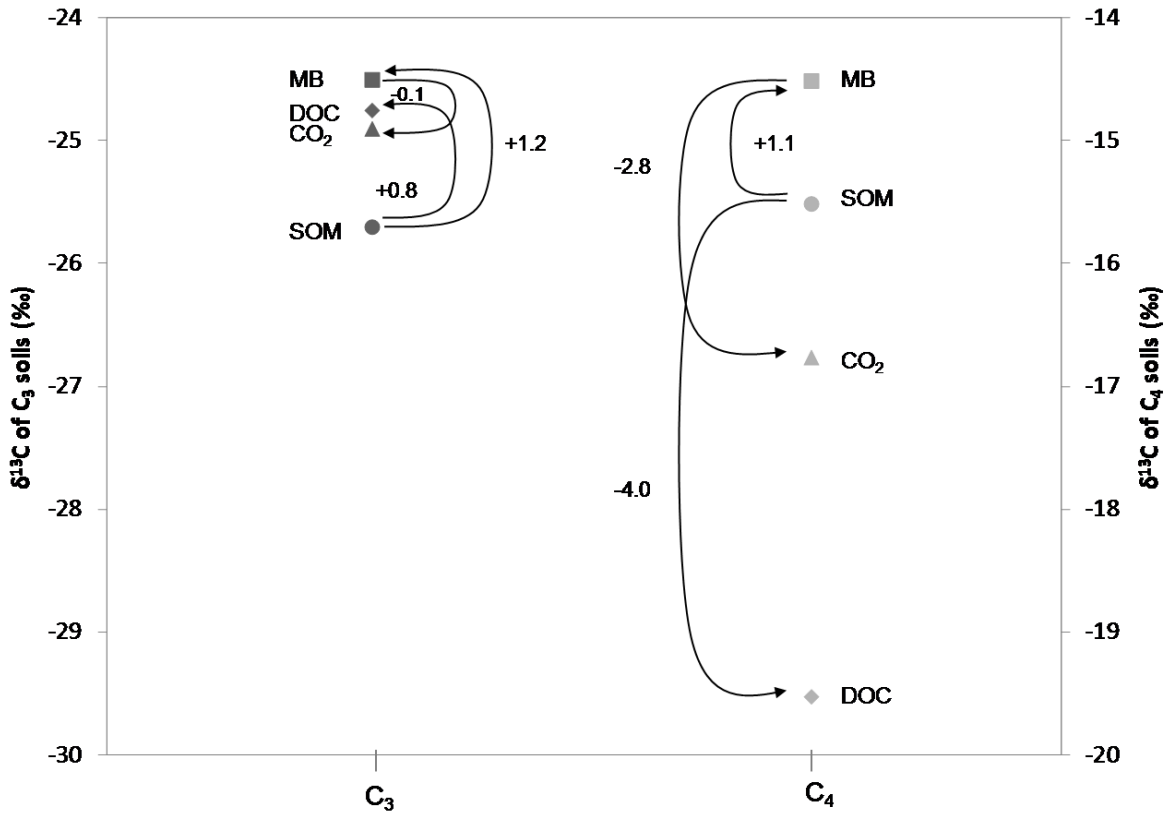


Figure 8.5 – ^{13}C discrimination processes between soil organic matter (SOM), and the soil carbon pools: DOC, microbial biomass (MB) and SOM-derived CO_2 for C_3 and C_4 soils (Werth and Kuzyakov, 2010)

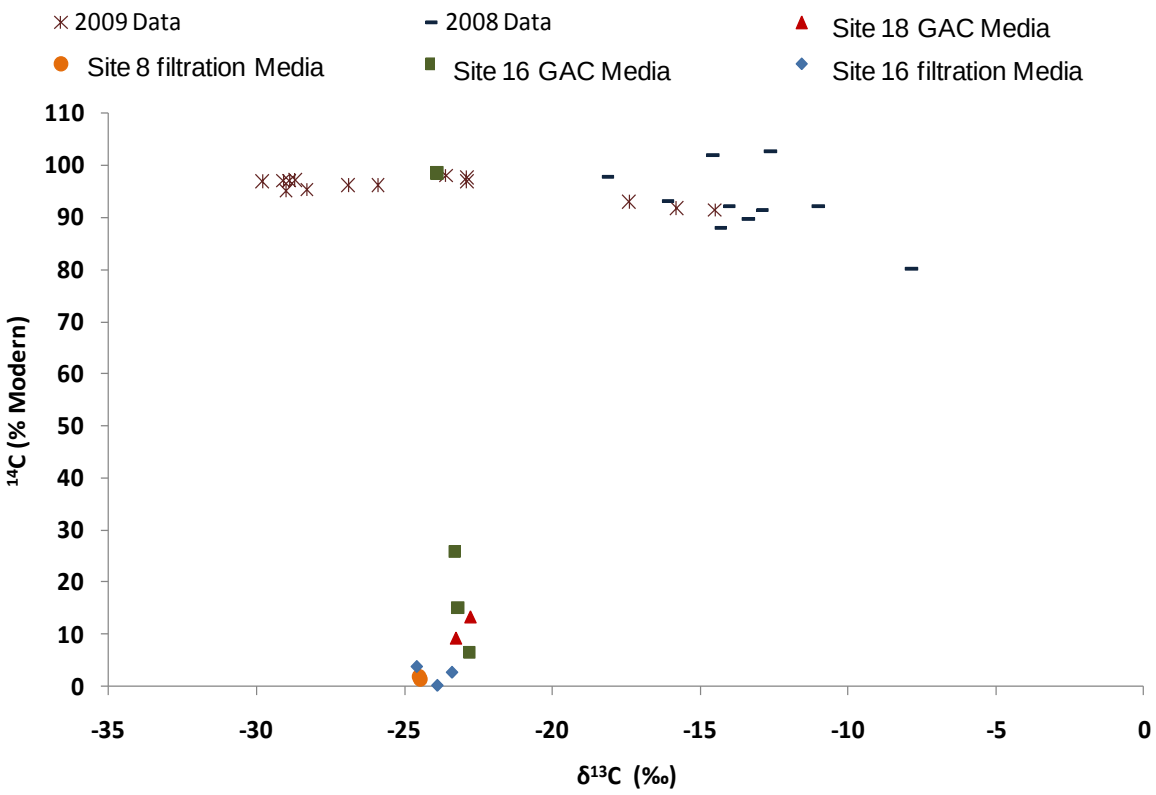


Figure 8.6 – GAC, filter media and standards data

Chapter 8 Tables

Table 8.1 – 2008 P-GAC sampling data

Site	Sampling date	^{14}C (% modern carbon)	^{14}C error (%mc)	^{14}C age years (AD)	$\delta^{13}C$ (‰) error 0.5‰	Peak C Intensity (AU)	Peak C Emission (AU)	Peak T Intensity (AU)	DOC $mg.l^{-1}$
Site 3	08/07/2008	80.26	0.37	1709	-7.86	48.2	408.0	22.2	1.9
	07/11/2008	88.00	0.41	969	-14.29	68.3	423.9	21.6	2.7
Site 5	07/07/2008	102.04	0.45	Modern	-14.57	66.6	422.0	21.7	2.7
	06/11/2008	102.67	0.47	Modern	-12.62	88.7	423.9	32.5	3.6
Site 2	07/07/2008	92.22	0.43	594	-14.00	49.1	410.0	12.8	2.0
	06/11/2008	92.16	0.40	598	-11.00	47.9	408.0	10.4	1.9
Site 13	07/07/2008	91.49	0.42	658	-12.90	78.0	418.0	23.5	3.1
	06/11/2008	97.81	0.43	121	-18.12	70.2	438.1	18.2	2.8
Site 16	07/11/2008	93.13	0.41	515	-16.10	113.9	422.0	22.8	4.6
Site 8	07/11/2008	89.77	0.41	809	-13.36	101.5	416.1	25.8	4.1

Table 8.2 – NOM characteristics and radiocarbon isotope composition through the treatment process

Site	Sample Point	UV_{254} ($Abs.m^{-1}$)	Turbidity (NTU)	TOC ($mg.l^{-1}$)	SUVA* ($L\,mg^{-1}\,m^{-1}$)	^{14}C (%mc) ± 1σ	δ^{13} ($‰_{V\text{-}PDB}$) ± 0.5‰
Site 8	Raw	19.7	0.8	4.1	4.9	91.46 ± 0.42	-22.7
	Post Clarification	11.9	1.1	3.2	3.7	97.10 ± 0.42	-28.9
	Post Filtration	12.3	0.1	2.9	4.2	95.35 ± 0.44	-28.3
	Post-GAC	7.7	0.1	2.4	3.2	97.26 ± 0.43	-28.7
	Post-GAC (unfiltered)	7.7	0.1	2.4	3.2	91.85 ± 0.42	-15.8
	Final	7.7	0.1	2.4	3.2	95.11 ± 0.44	-29.0
	Final (unfiltered)	7.7	0.1	2.4	3.2	93.12 ± 0.43	-17.4
Site 16	Raw	19.7	1.4	7.2	2.8	98.10 ± 0.43	-23.6
	Post Clarification	10.4	0.4	6.0	1.7	96.99 ± 0.45	-29.8
	Post Filtration	10.2	0.3	5.3	1.9	96.21 ± 0.44	-25.9
	Post-GAC	9.3	0.2	3.6	2.6	97.14 ± 0.45	-29.1
	Post-GAC (unfiltered)	9.3	0.2	3.6	2.6	97.65 ± 0.45	-22.9
	Final	4.1	0.1	3.7	1.1	96.27 ± 0.42	-26.9
	Final (unfiltered)	4.1	0.1	3.7	1.1	97.06 ± 0.45	-22.9

*Specific Ultraviolet Absorbance Units

Table 8.3 – NOM fluorescence characteristics through the treatment process

Site	Sample Point	Peak C Emission (AU)	Peak C Intensity (AU)	Peak T Intensity (AU)
Site 8	Raw	421.9	119.5	35.6
	Post Clarification	441.9	109.1	32.2
	Post Filtration	413.9	105.5	31.7
	Post-GAC	420.0	85.8	20.8
	Post-GAC (unfiltered)	422.0	83.3	20.7
	Final	420.0	78.9	18.9
	Final (unfiltered)	425.9	76.6	18.7
Site 16	Raw	418.0	183.8	69.8
	Post Clarification	426.1	135.8	52.9
	Post Filtration	413.9	134.1	53.6
	Post-GAC	426.1	39.5	11.9
	Post-GAC (unfiltered)	418.1	38.6	13.9
	Final	420.0	24.3	6.6
	Final (unfiltered)	412.9	23.8	7.6

Table 8.4 – GAC and filtration media ^{14}C & $\delta^{13}C$ signatures, sampled November 2009

Site	Sample	Sample description	^{14}C (%mc)	Conventional radiocarbon age (years)	$\delta^{13}C$ (‰)
Site 8	GAC Media	3 months since regeneration	9.34 ± 0.11	19040 ± 102	-23.27
	GAC Media	9 months since regeneration	13.37 ± 0.12	16159 ± 73	-22.77
	Filter media	Anthracite grade 2	1.41 ± 0.11	34181 ± 677	-24.45
	Filter media	Sand 450mm	1.86 ± 0.11	31971 ± 512	-24.50
	Filter media	Garnett	1.71 ± 0.11	32678 ± 559	-24.14
Site 16	GAC Media	GAC virgin coal	6.46 ± 0.12	22004 ± 147	-22.8
	GAC Media	11 months since regeneration	15.09 ± 0.13	15189 ± 71	-23.2
	GAC Media	Coconut trial media	98.61 ± 0.43	112 ± 35	-23.9
	GAC Media	2 weeks since regeneration	25.80 ± 0.15	10884 ± 47	-23.3
	Filter media	Anthracite grade 2	0.07 ± 0.12	Background	-23.9
	Filter media	Sand 450mm	2.61 ± 0.12	29297 ± 365	-23.4
	Filter media	Gravel filter media	3.73 ± 0.12	26416 ± 256	-24.6

Chapter 9. Analysis of colloidal material through a water treatment works

9.1 Introduction

Colloids and environmental nanoparticles play an integral role in contaminant binding and transport of pollutants in water systems (Baalousha and Lead, 2007) prompting concerns for their effective removal during treatment. Environmental nanoparticles are also thought to affect inorganic colloidal stability, with fulvic substances stabilising through charge modification and colloidal aquagenic organic carbon accelerating coagulation processes (Wilkinson et al., 1997a). Although there is an increasing amount of research into colloids and nanoparticles, their structural characteristics and their role in environmental systems, there is a complete knowledge gap in the characterisation of environmental nanoparticles through the water treatment process. Improvements in colloidal characterisation techniques have also advanced significantly over the previous 10 years, so techniques are able to provide more in-depth analysis of samples with increased certainty. It is therefore suggested that the improved sensitivity of colloidal characterisation techniques could provide an additional perspective to NOM analysis that is not already provided by existing characterisation techniques.

This final investigative chapter focuses on objective (ii):

To investigate the potential for carbon isotopic analysis and environmental colloidal analysis as NOM characterisation tools, to address current characterisation needs and to identify trends with DBP formation.

In order to address this objective leading colloidal and nanopartide investigation technology was utilised for NOM characterisation and interaction through water treatment with respect to DBP formation. In particular, investigation focused on the effect of specific treatment stages on colloid and environmental nanoparticle character and concentration. The use of colloidal and nanoparticle analysis therefore aimed to address the following questions;

- Can colloidal characterisation techniques such as atomic force microscopy (AFM), dynamic light scattering (DLS) and nanoparticle tracking analysis (NTA) characterise NOM at 5 contrasting surface water treatment sites.
- How does colloidal analysis compare to existing characterisation methods?
- Using colloidal analysis techniques, is NOM affected by individual water treatment processes, and how?
- Is there a link between environmental colloidal parameters and DBP formation?

In order to meet these research needs, experimental design focused on sampling from five WTWs of varying NOM character were selected in the Midlands region of the UK; Site 1, Site 5, Site 8, Site 13 and Site 16. Samples of raw, post-clarification, post-filtration and post-GAC waters were fractionated by 1 µm, 0.45 µm, 0.22 µm and 0.10 µm filters. NOM characterisation was performed using fluorescence spectroscopy, UV_{254}, TOC and NTU. Colloidal size distribution analysis, surface interactions and composition investigations were

performed on the 0.10 µm fraction using a variety of techniques, including; Dynamic Light Scattering (DLS), Nanoparticle Tracking Analysis (NTA) and Atomic Force Microscopy (AFM).

9.2 Colloidal characterisation of raw surface waters

As mentioned in earlier chapters, the raw water qualities from the chosen five sites differ greatly in their composition of organic matter. Sites Site 5 and Site 16 are typically described as having poor removal due to an enrichment of difficult to remove HPI. The dominance of HPO in Site 1 source waters and ease of removal contrasts significantly to the aforementioned sites. It would therefore be expected that any distinctions in results would be between these three sites. Typical NOM characterisation between sites for this investigation can be seen in figure 9.1 for reference.

Colloidal characterisation techniques such as DLS, NTA and AFM were chosen for the specific products they offer. DLS is a method of assessing particle size and hydrodynamic diameter – how a particle diffuses in a liquid. It is also a method of measuring aggregation potential. DLS was chosen as it is a rapid technique, providing a number of usable outcomes per sample. It also uses equipment that is already available at Severn Trent – the DTS Nano used for zeta potential measurements. NTA is an imaging technique providing size and shape measurements as well as an image of the particle surface and was chosen for the detailed images of particle shape, in order to show how particle shape changes through treatment and if this has any impact on removal or DBP formation. Finally, AFM is another measure of particle size and quantity, and is also able to provide information on particle

variation. AFM was chosen to compare with DLS measurements, and when combined with NTA< it can provide information on the mean and smallest particle sizes within a sample.

Fluorescence intensity of Peak C has been previously been proven to be a reliable indicator of TOC removal (Bieroza, 2009). TOC values in table 9.2 for Site 16 and Site 5 lie within very similar ranges (5.47-5.63 mgL^{-1} and 5.52- 5.70 mgL^{-1} respectively) however peak C fluorescence intensities displayed in figure 9.2 contrast significantly. Fractionation profiles of raw waters as seen in figure 9.2 give little indication as to an explanation for this, however HPO is higher at Site 16 but not in as greater quantities as seen at Site 1 (7.01-8.27 mgL^{-1}). At Site 16 and Site 5, individual size fraction fluorescence intensities follow comparable patterns, with the 1.00 µm size fraction exhibiting the greater fluorescence intensity, followed by the smallest size fraction, 0.10 µm. Site 13 raw waters also demonstrate the observed pattern. Using figure 9.3 for reference, organic material within the 1.00 µm size range would typically consist of polysaccharides, peptidogylcans and cellular debris. Humic and fulvic material would predominantly be in the 0.10 µm size fraction, although humic aggregates could be present up to 0.45 µm. The greatest fluorescence intensity recorded for Site 1 raw waters was within the 0.10 µm fraction, followed by 0.22 µm. Site 8 raw waters suggest a similar pattern, although the 0.22 µm fraction has the greatest fluorescent intensity. Results suggest that for all sites, the standard recordings of fluorescence intensity after filtering through a 0.45 µm membrane is underestimating fluorescence intensity signatures for NOM.

NTA hydrodynamic diameter and AFM mean particle size provide an indication of particles sizes in the 0.10 µm samples and results can be seen in table 9.2. NTA hydrodynamic

diameter records the average size of the particles in the sample, whereas AFM mean particle size refers to the smallest observed particle size. Site 5 raw water has the smallest particles at 11.60 nm, with a minimal error. NTA measurements are higher at 78.00 nm suggesting a range of colloidal sizes present.

Site 13 raw waters display the largest range of colloidal material, which is expected as Site 13 is a direct river extraction site whereas the remaining sites have some form of settling reservoir before being pumped into the works. All samples were filtered through a 0.10 µm membrane, equivalent to 100.00 nm, so with NTA values at 196.00 nm there has already been substantial aggregation between the colloids. Colloidal NTA values at Site 1 also display signs of aggregation with an average particle size of 111.00 nm. With the inclusion of error bars, Site 8 and Site 16 raw waters have an overlap between AFM and NTA measurements, indicating colloidal organic matter is of a consistent size throughout the sample. Values also suggest that colloids in Site 8 and Site 16 samples are relatively stable and unlikely to be aggregating to the same degree as seen at Site 1 and Site 13 or electrostatic forces are less, resulting in fewer successful collisions.

DLS hydrodynamic diameter measurements are again a measure of particle size, however due to the nature of the particle measurement procedure, any larger particles present in the sample are given a higher weighting in the average particle size, thus not giving a representative value for particle size. In such case, DLS hydrodynamic diameter measurements are an excellent indication of the aggregation potential of colloidal material. Figure 9.4 shows raw water for all five sites is clustered below 500 nm.

9.3 Colloidal characteristics through water treatment

In figure 9.5 DLS measurements through the treatment process show the addition of coagulant dramatically increases colloid aggregation potential. Site 1 DLS measurements increase the most, from 150.00 nm to 1900.00 nm. This is closely followed by Site 8 which increases from 349.00 nm for raw water to 1650.00 nm post-clarification. Both sites are located in the Peak District, known for its organic rich peaty soils. The elevated aggregation potential of these two sites could be attributed to the high fulvic content of source waters. Site 5 and Site 16, two typically lowland and HPI-rich sites are the least affected by the addition of coagulant and subsequently have the lowest DLS hydrodynamic diameter measurements at 708.00 nm and 532.00 nm respectively. Post-filtration samples show a reduction in hydrodynamic diameter for all sites except Site 1. This could be attributable to the removal of particulate material in filtration. Hydrodynamic diameters once again increase after the final treatment stage, GAC, with sample sites discriminated by organic matter composition with lowland HPI-rich sites having the lowest DLS measurements.

AFM and NTA measurements through the water treatment process (figure 9.6) show reductions in average particle sizes after clarification for all sites except Site 8, signifying the removal of larger particles. Large error bars at Site 8 however imply the NTA measurement post clarification is uncertain. Post filtration, average particle sizes are again decreasing for most sites, excluding Site 1, although reductions are slight. Increases in average particle size post-GAC are also evident at most sites, symptomatic of the removal of smaller colloidal matter. AFM results are somewhat more difficult to interpret. AFM results are supplemented by AFM images for each sample, seen in figures 9.8 to 9.12. At Site 5, post-

clarified particles appear to agglomerate together but a wide range of particle sizes are still apparent. The smaller particles (<1 nm) have been removed through filtration, but particles are larger and more angular. Post-GAC, particle sizes are once again reduced having being either broken up or removed. Figures for percentage TOC removal (table 9.3) show a reduction of 18.38% post-GAC, implying the removal of the larger colloids in the 0.10 µm fraction. This is also evident at Site 13, where percentage TOC removal by GAC is higher at 23.44%. Results for Site 16 (figure 9.13) contradict this with an increase in both AFM and NTA, and AFM images showing the presence of larger, circular particles. Percentage TOC removals of 39.59% in the 0.10 µm fraction are unusual for Site 16, with figure 9.13 showing a significant removal of the HPINA fraction. AFM images show particles appear mainly spherical, with one rod-like particle present post-GAC.

Percentage Peak C intensity removal for post-clarification shows a greater percentage fluorescence reduction in the <0.10 µm fraction for Site 5, Site 13 and Site 8 waters (figure 9.13). The 0.22 µm fraction appears to be the least amenable to coagulation/flocculation and clarification. The 0.22 µm fraction could consist of humic aggregates which, having already aggregated could be unresponsive to coagulation/flocculation processes but too small settle out of suspension. Filtration processes for each site removes particles sizes indiscriminately, with the main reduction in peak C intensity from coagulation/flocculation and GAC. Individual and cumulative percentage TOC reductions displayed in table 9.3 show Type 1 waters (high HPI content) have the least percentage removal of the 0.10 µm fraction, whereas Type 2 waters Site 13 and Site 8 have greater percentage TOC reductions in the 0.22 µm for Site 8 and 0.10 µm fraction for Site 13. The larger smaller particle removals come from the final GAC treatment phase. Trends in percentage TOC reductions differ from

percentage peak C intensity removals suggesting the smallest size fractions have higher fluorescence intensities than the larger particles. This correlates with the size ranges of humic and fulvic material shown in figure 9.3, but suggests that the smaller size ranges are not being removed through coagulation and flocculation processes and potentially overloading GAC columns.

9.4 Relationships between environmental colloids and DBPs

TTHMFP results displayed in figure 9.14 show an increase in TTHMFP after treatment for all sites except Site 1. Although many sites achieve good removal, for example Site 16 removes up to 72% of TOC; there is a substantial increase in THMFP such as bromodichloride and chlorodibromide. Removal of precursors for chloroform is evident at Site 1 and Site 16, with both sites achieving considerable removal of the 1.00 µm and 0.45 µm size fractions. Incidentally, Site 8 WTW sees significant increases in chloroform formation potential, which could be linked to the poor overall removal of HPO organics, as seen in figure 9.2, a strong argument for optimisation of removal processes. Actual THM produced for the five sites show similar patterns in the increase in THM post-GAC for Site 8 and Site 13, and the considerable increase in chlorodibromide and bromodichloride at Site 1. Although Site 1 removes a sizeable percentage of HPO (90.96%), it fails to make a significant reduction in HPIA, removing only 26.24% (table 9.4). The increase in chlorodibromide, bromodichloride and chloroform at Site 13 could be attributed to the minimal reductions of 13.85% and 16.67% for HPIA and HPINA respectively. It is therefore assumed that chemical alteration of particles during water treatment is causing an increased production of THM such as chlorodibromide and bromodichloride, whilst the HPO is the main precursor for chloroform.

Correlations between THM and traditional organic matter characterisation tools such as fluorescence and TOC (table 9.5) showed strong correlations between the smaller size fractions (0.22 µm and 0.1 µm) for chloroform, chlorodibromide (THMFP) and TTHMFP/TOC and peak C emission wavelength. The TTHMFP/TOC correlation with the 0.10 µm size fraction could be particularly useful for the rapid prediction of TTHMFPs on a WTW (figure 9.15). Interestingly, the most commonly used fraction, 0.45 µm showed no correlation for either THMFPs or THM. Bromodichloride formation potential correlated well with peak T intensity, and as figure 9.16 shows, bromodichloride is the second largest THMFP identified in P-GAC waters for all sites. The strongest correlation is at 0.45 µm (0.87 r^2), but any size fraction could be used. TOC is also strongly correlating with TTHMFP and chloroform at 0.86 r^2 and 0.83 r^2 respectively. Figures 9.16 to 9.18 display the strongest correlations, however it is worth noting that due to the small number of samples, relationships could not be confirmed as stastically significant and correlations could reduce with an increased sample size.

When analysing for relationships between NTA, DLS and AFM techniques with DBP formation, there was a distinct lack of correlation between any of the variables and either actual or potential THM formed. Within the <0.1 µm fraction, it therefore insinuates that particle size at these sites has little impact on the number of DBP formed. It is worth noting however that sample size would have been a significantly limiting factor in the investigation.

Correlations between ICP-MS analysis and THM reveal that the dissolved fraction of organic material is not significantly influencing THM production at these sites, however metals

absorbed onto the colloidal fraction gave many strong correlations with THM and THMFPs, reinforcing the view that colloidal size enhances reactivity. Aluminium, chromium and iron are linked most strongly to chloroform and total THM and THMFPs. It is possible that the ferric (Fe^{3+}) used in coagulation could be contributing quantities of iron, however aluminium is used at only one of the five sites. Chromium and iron relationships are still high with total organic material though this is most likely influenced by relationships in the colloidal fraction.

Comparing the use of colloidal characterisation techniques with existing NOM characterisation techniques for the use of DBP precursor identification or prediction indicate existing techniques are more successful in identifying links with DBP formation. The techniques used for colloidal characterisation are largely based on particle size and shape, whereas techniques such as UV and fluorescence are a measure of particle excitation and absorbance. The type of material at the <0.1 µm size range would also have an impact, as this material is typically HPI material with little or no charge density. In this instance, colloidal characterisation techniques such as DLS, NTA and AFM are unable to provide additional information of DBP formation or precursors.

9.5 Discussion

Research into the fate of natural environmental colloids in surface waters is becoming increasingly popular and subsequently, significant improvements have been made to the sensitivity of analytical techniques for colloidal analysis (Baalousha and Lead, 2007, Buffle and Leppard, 1005). The increasing use of such techniques in colloidal characterisation

studies and with research stating that environmental colloids are highly reactive and influence the fate and behaviour of trace pollutants in natural waters (Newman et al., 1994, Lead and Wilkinson, 2006) and the need for the identification of HPI NOM in surface waters and links between occurrence and the formation of DBP, it was wise to consider the use of colloidal characterisation techniques for NOM characterisation.

DLS is a non-invasive technique used for characterising macromolecules in solution and particles in suspension. It provides information on particle hydrodynamic diameter, particle size and particle aggregation potential. When using the technique, very little sample preparation was required, and the instrument is simple to use. Particle size information was however deemed to be extremely misleading, as the average particle size measurement is was significantly skewed by larger particles in the sample. Although samples were filtered through a 0.1 µm membrane, particles were found to agglomerate quickly to form particles of upward 500 nm. The DLS software placed a higher weighting in the mean sample size calculation on this particle, so an unrepresentative result was produced. The aggregation potential measurements did however provide an interesting, and previously unseen contrast between sites, which were linked to NOM composition.

NTA is used for particle size and number information. Again, the sample required little preparation before being analysed, and the NTA software provided very comprehensive results on the mean particle size, number and particle size distribution. This again provided a unique insight into the fate of environmental colloids through water treatment, however it is unlikely this technique would be suitable for on-site analysis as it is very sensitive equipment. One issue that was encountered during the analysis was due to particle

number. Once the sample was filtered through a 0.1 µm membrane and injected into the viewing unit, there were only a very limit number of particles recorded – especially with post-GAC and final samples. On a number of occasions, the instrument found it difficult to identify many particles.

AFM analysis is also a measure of particle size, but it also used for the imaging of particles. In colloidal research, NTA and AFM results generally compliment each other (lead and Wilkinson, 2006, Baalousha and Lead, 2007). During this study this was generally the case, however there was variation between the two measurements on a number of occasions. AFM uses minute forces to measure particle size, whereas NTA uses laser light to illuminate particles and tracks the Brownian motion of particles. This results in NTA analysis measuring the average particle size and AFM recording the smallest particle. Particle images produced provided further comparison between particles size and shape, however it is unlikely this data would have a significant impact on the potential of current treatment processes.

When comparing colloidal characterisation methods to existing NOM characterisation methods, in terms of characterising OM with respect to DBP formation, colloidal characterisation techniques would be unable to add information regarding reactivity of particles. They would however provide a new perspective on the fate of colloids though water treatment, which could be developed into a useful monitoring tool for process performance.

9.6 Conclusions

Colloidal characterisation techniques were successfully used to establish variation between the character of NOM at five contrasting surface water treatment sites. Colloidal characterisation techniques were used to provide information on the size, shape, polydispersity and aggregation potential of colloidal material in raw waters and through the WTW.

DLS measurements showed raw waters in the Severn and Trent catchments are typically very polydisperse and are prone to aggregation. The addition of coagulant promoted the reduction of electrostatic repulsion, promoting successful collisions, however although the colloidal fraction is aggregating and forming larger particles, they are still too small to settle out of suspension.

AFM and NTA provide useful information on colloid size, aggregation potential and polydispersity, whilst AFM images give a clear indication of colloid shape through the water treatment works. This is also the first time that such techniques have been employed through the water treatment process. AFM images show water treatment processes destabilize particles, increasing their aggregation potential and altering colloidal shape.

Colloidal characterisation techniques were however unable to provide significant links to DBP formation or precursor identification at the five sites, and their use as rapid analysis tools of NOM character would also be limited.

Chapter 9 Figures

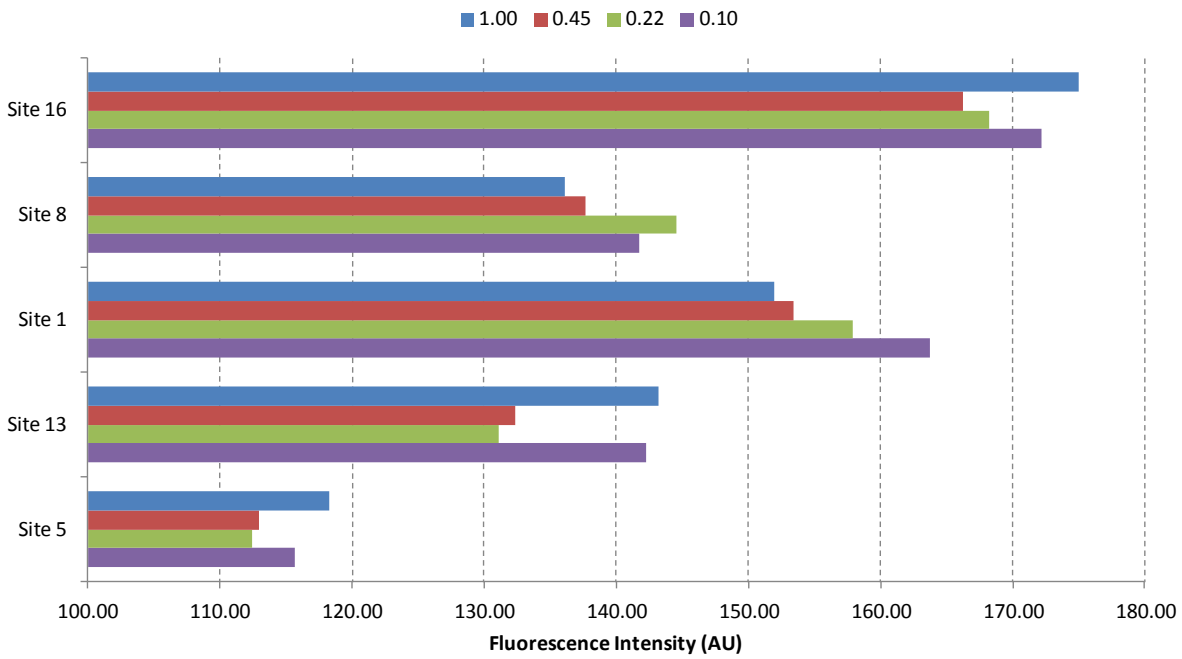


Figure 9.1 – Raw water Peak C Fluorescence intensity; key indicates size of membrane used for sample preparation (µm)

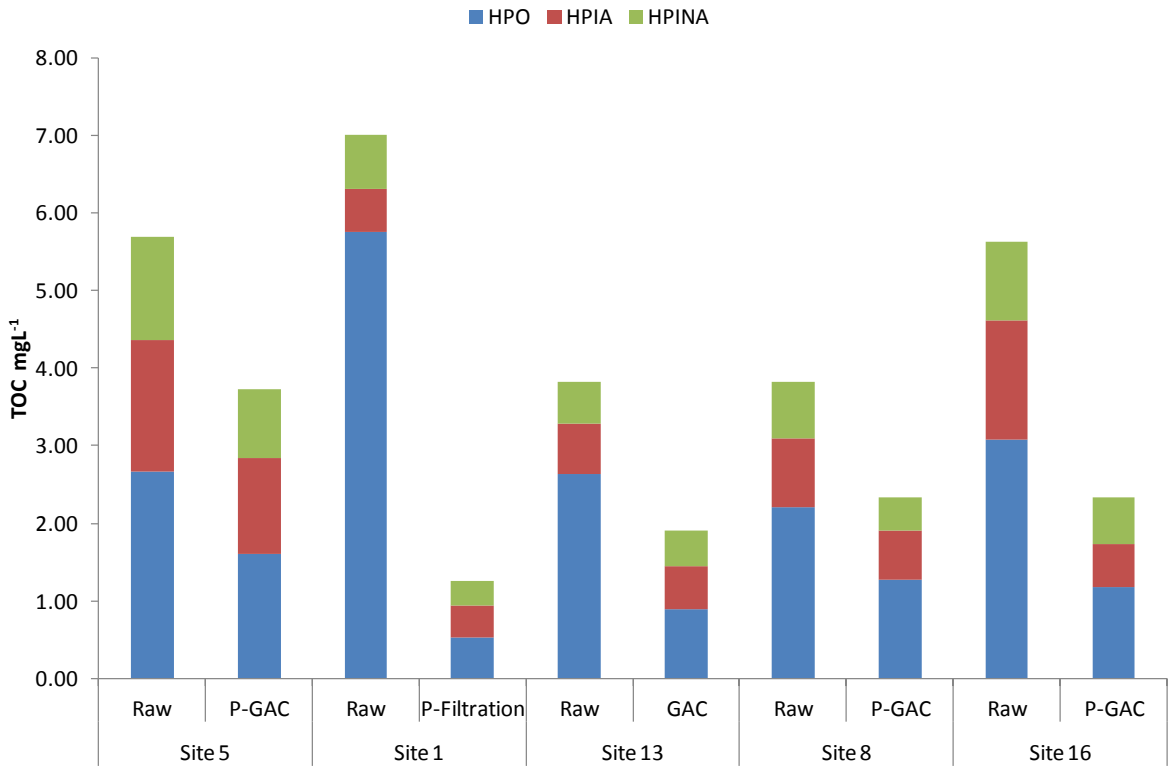


Figure 9.2 – Fractionation data on raw and treated waters

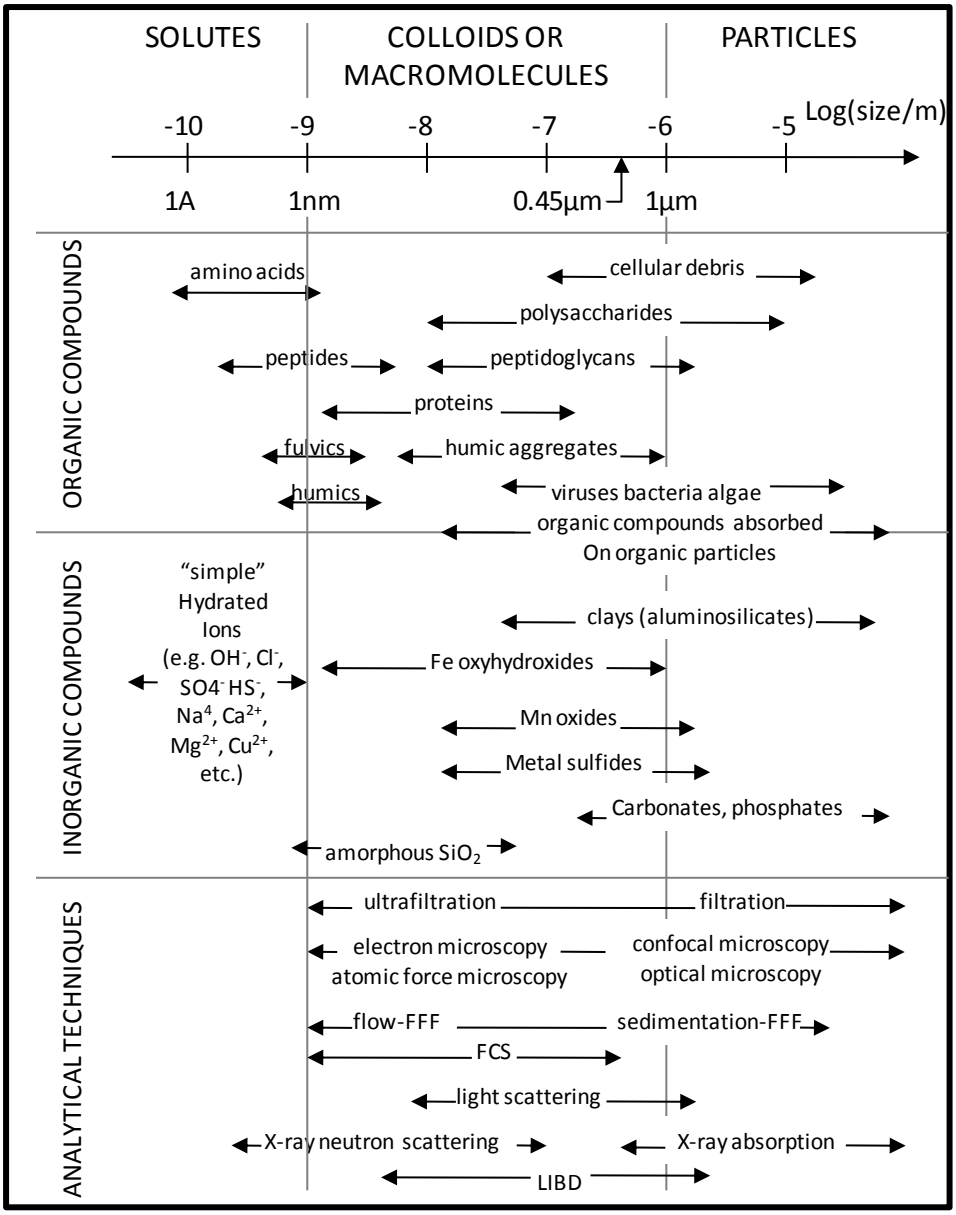


Figure 9.3 – Size range distribution (Ju-Nam and Lead, 2008)

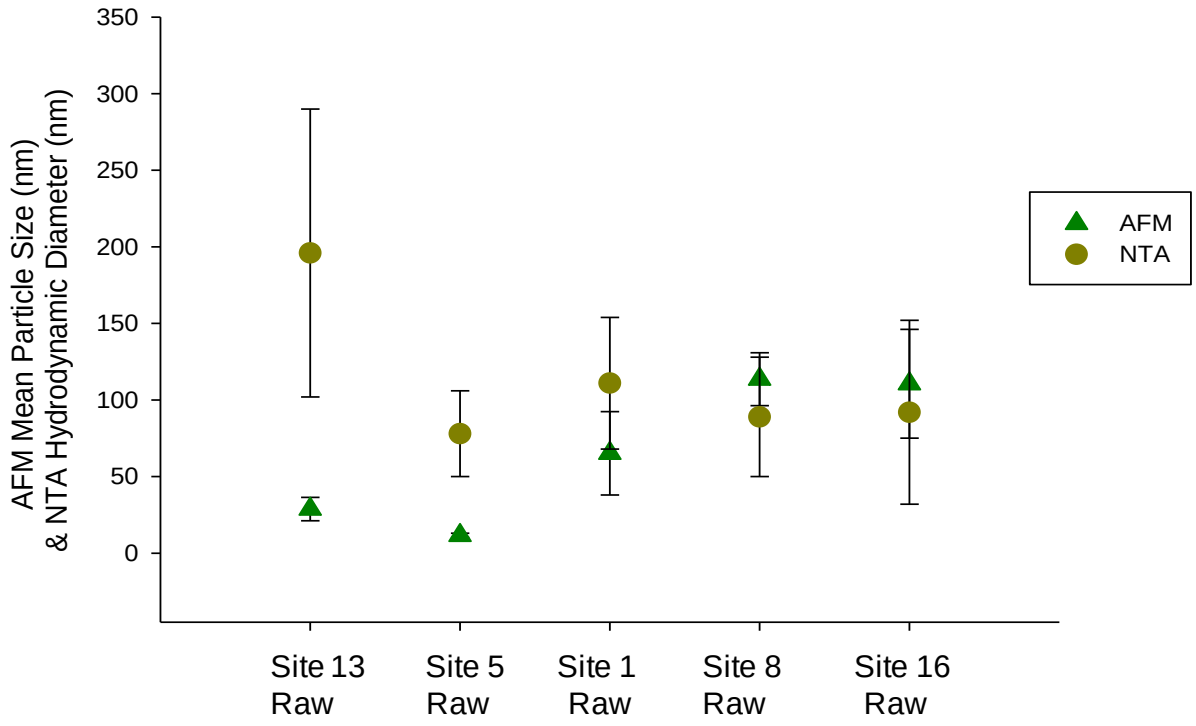


Figure 9.4 – Raw water colloid diameter

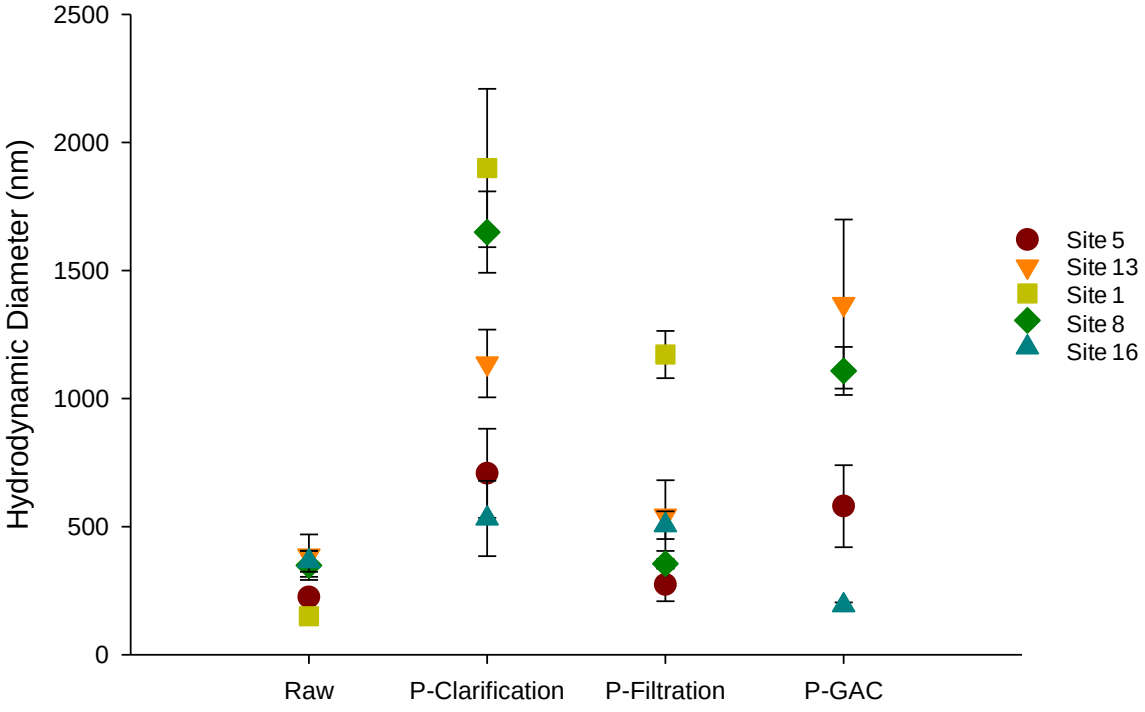


Figure 9.5 – DLS aggregation potential through treatment processes

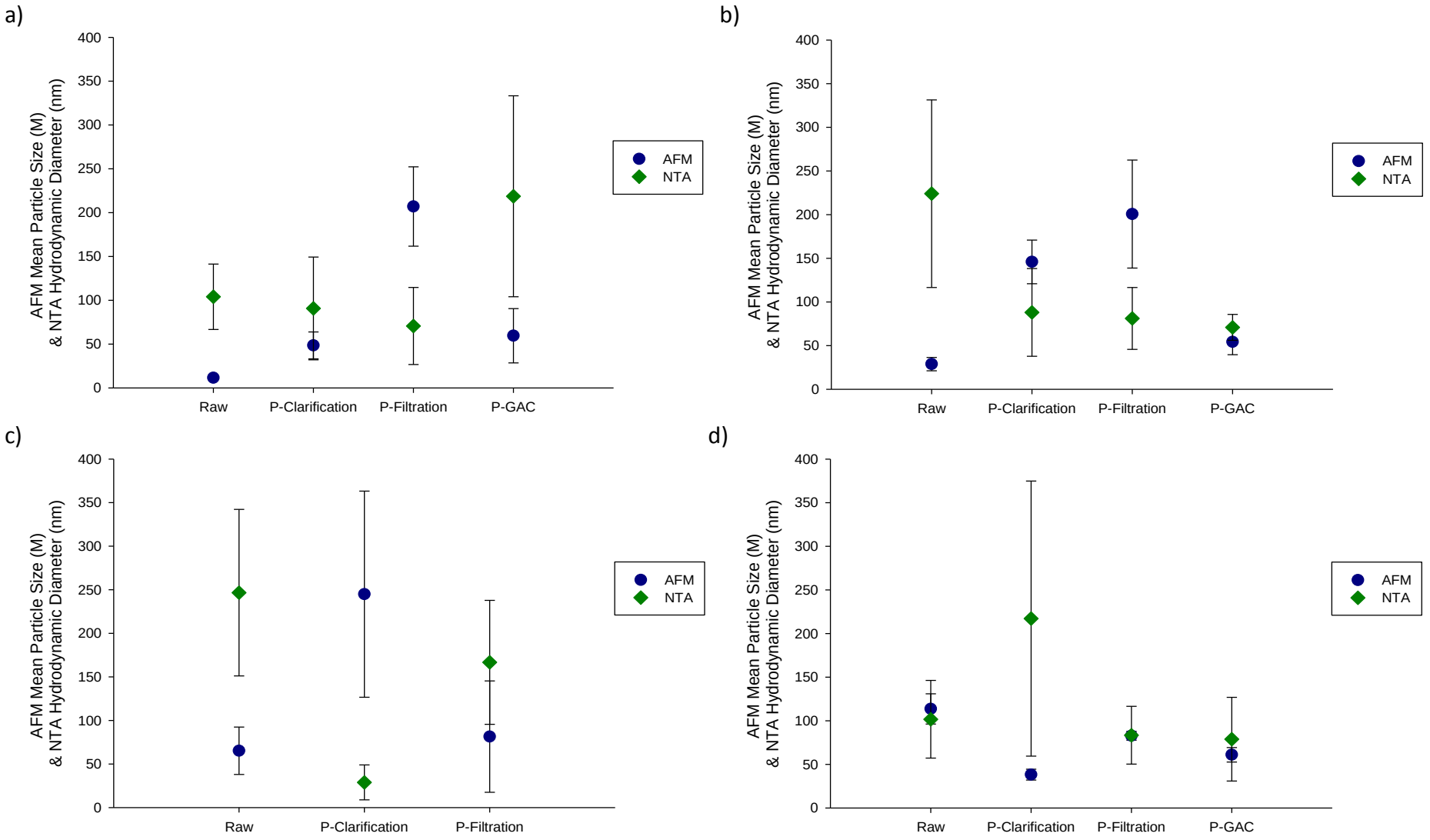
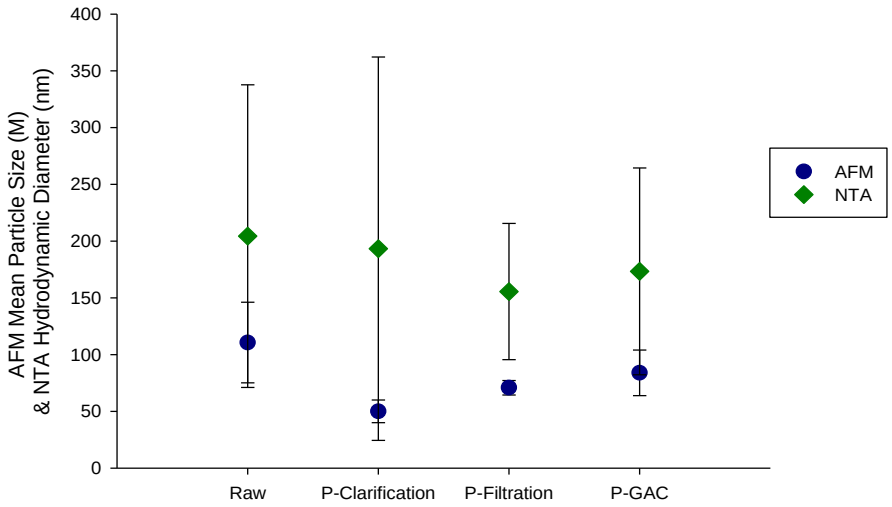


Figure 9.6 – AFM and NTA colloidal particle measurements for; a) Site 5, b) Site 13, c) Site 1, d) Site 8 & e) Site 16

e)


AFM Mean Particle Size (M)
& NTA Hydrodynamic Diameter (nm)
400
350
300
250
200
150
100
50
0
Raw
P-Clarification
P-Filtration
P-GAC
AFM
NTA

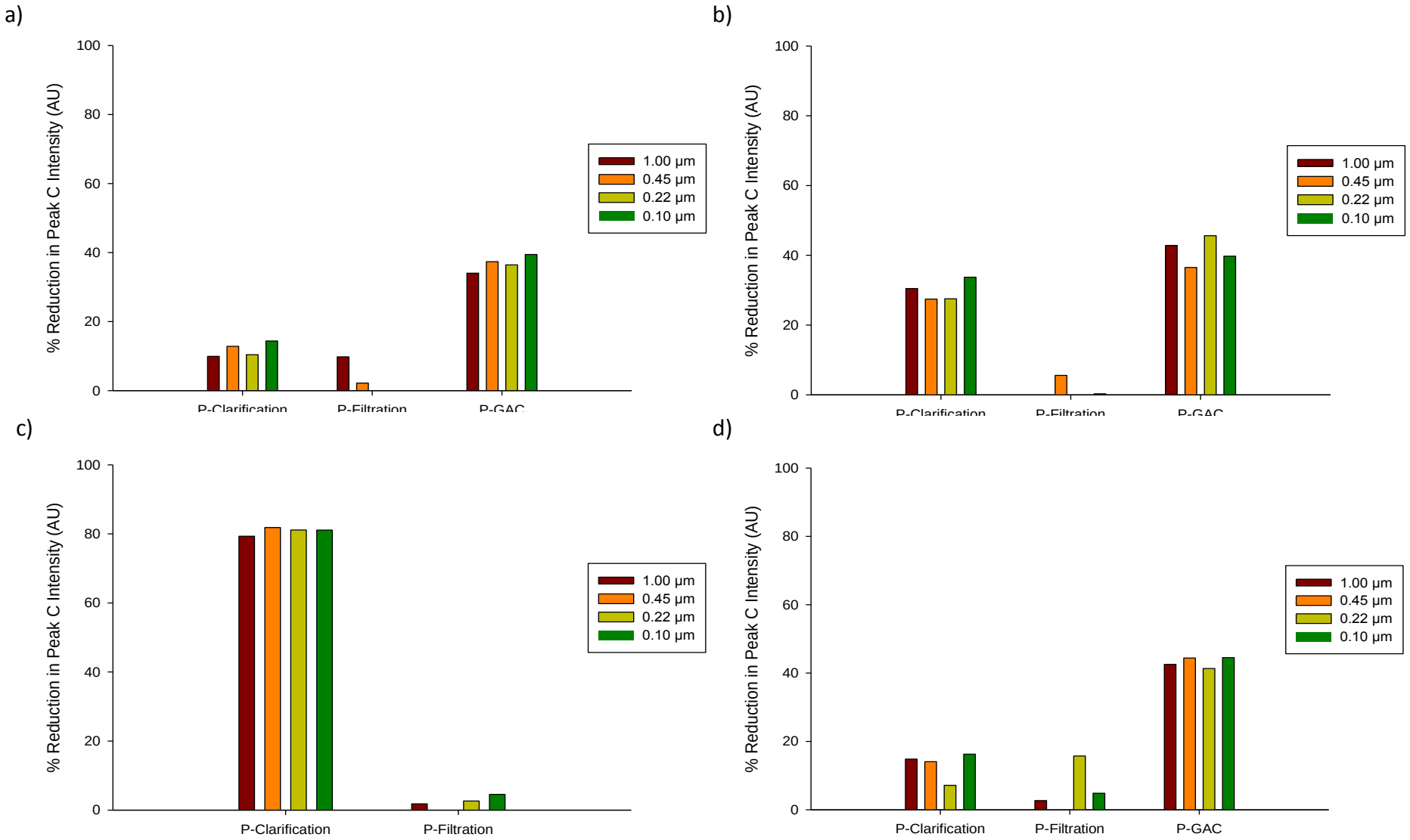
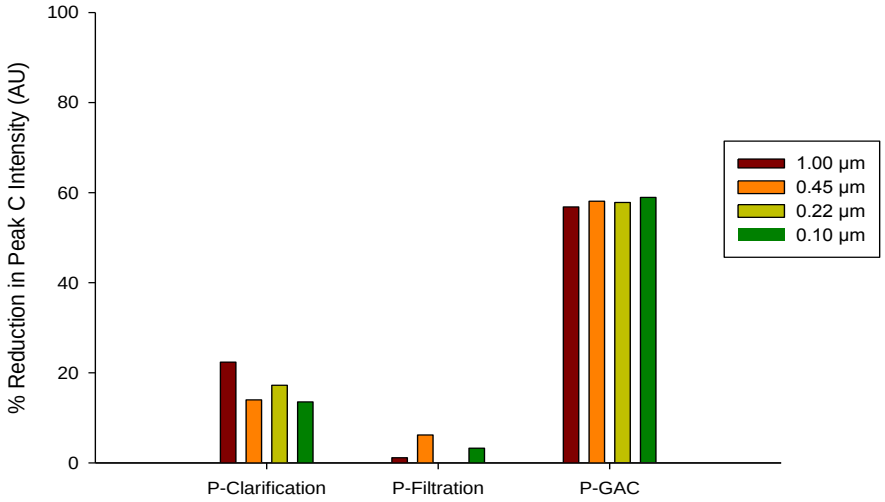


Figure 9.7 – Percentage Peak C intensity removal for sites; a) Site 5, b) Site 13, c) Site 1, d) Site 8 & e) Site 16

e)


100
80
60
40
20
0
% Reduction in Peak C Intensity (AU)
1.00 µm
0.45 µm
0.22 µm
0.10 µm
P-Clarification
P-Filtration
P-GAC

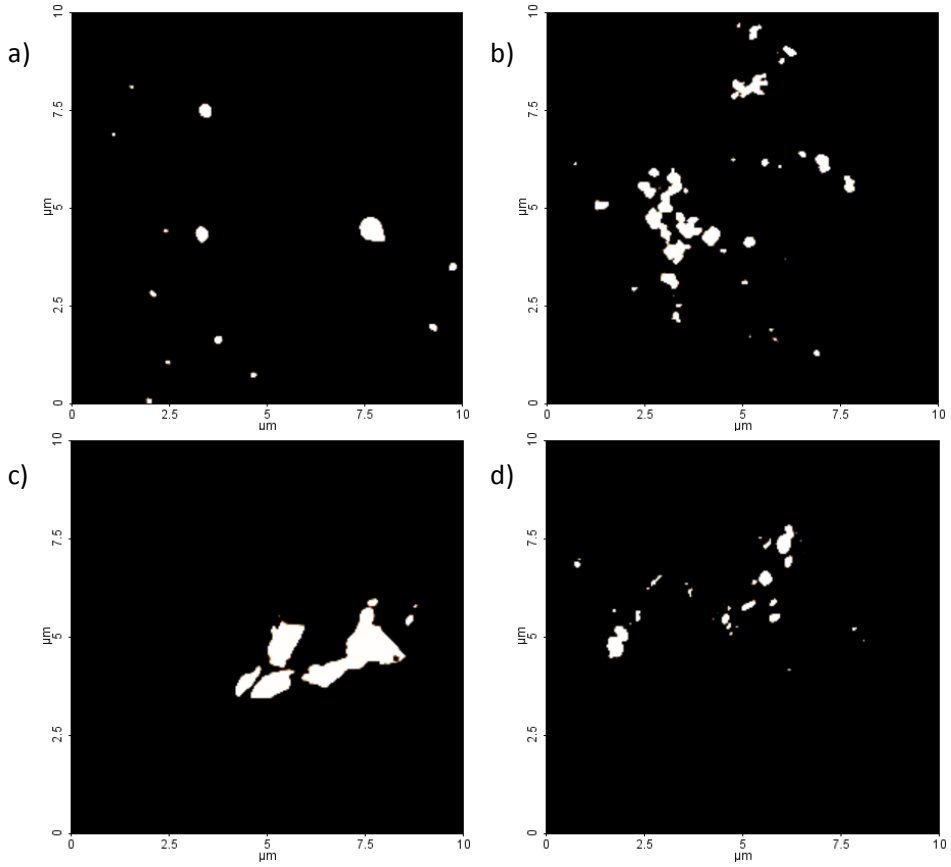


Figure 9.8 – Site 5 AFM images through treatment stages; a) Raw, b) clarified, c) filtered & d) post-GAC

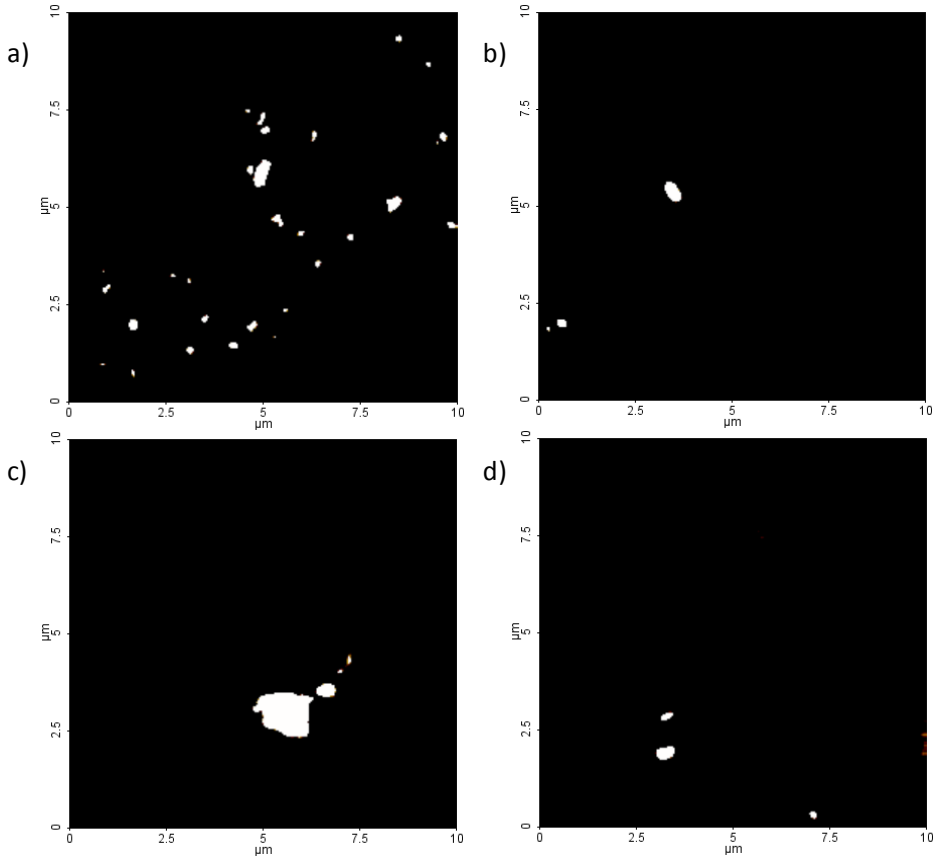


Figure 9.9 – Site 13 AFM images through treatment stages; a) Raw, b) clarified, c) filtered & d) post-GAC

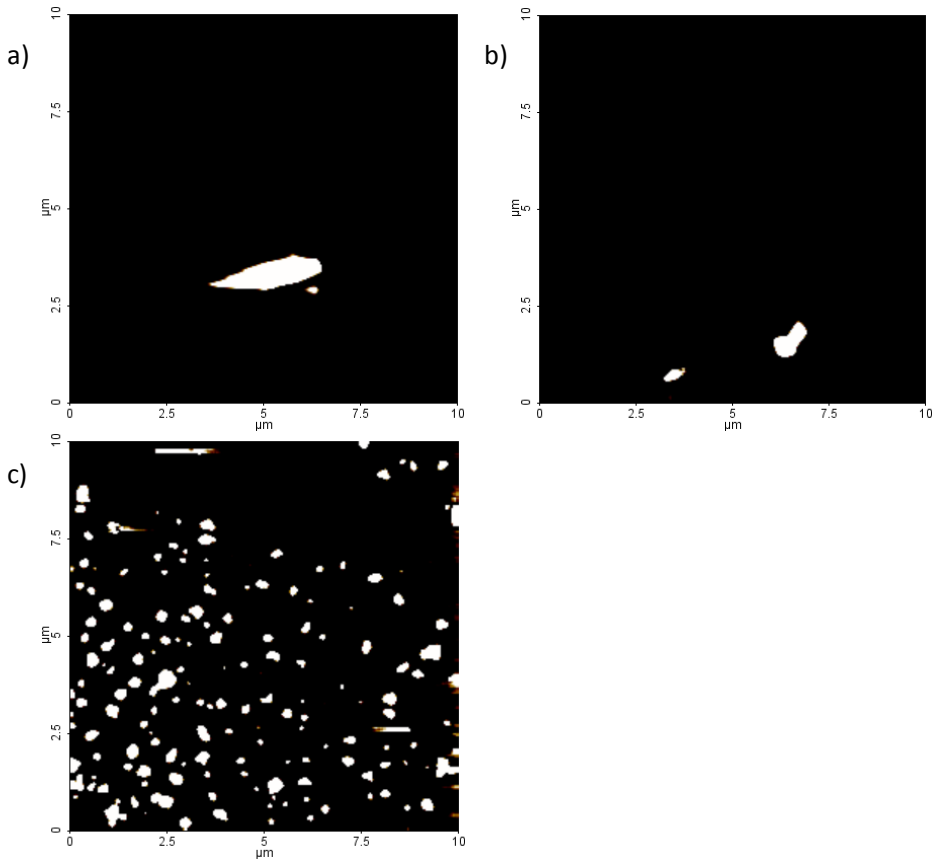


Figure 9.10 – Site 1 AFM images through treatment stages; a) Raw, b) clarified, c) filtered & d) post-GAC

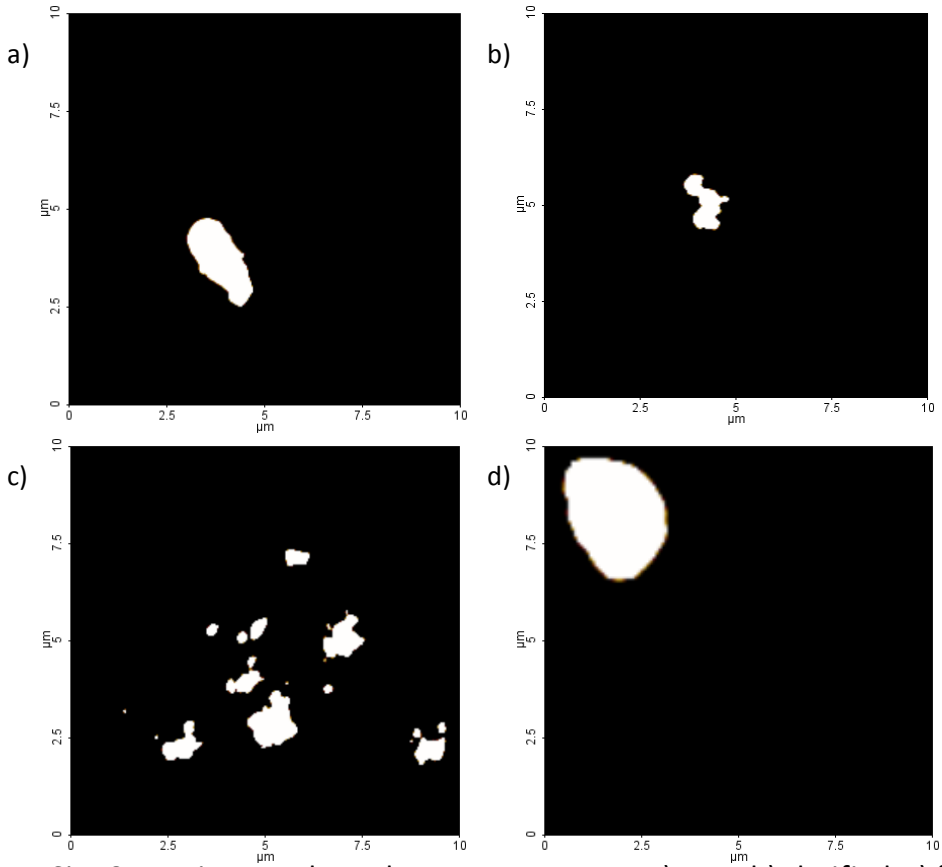


Figure 9.11 – Site 8 AFM images through treatment stages; a) Raw, b) clarified, c) filtered & d) post-GAC

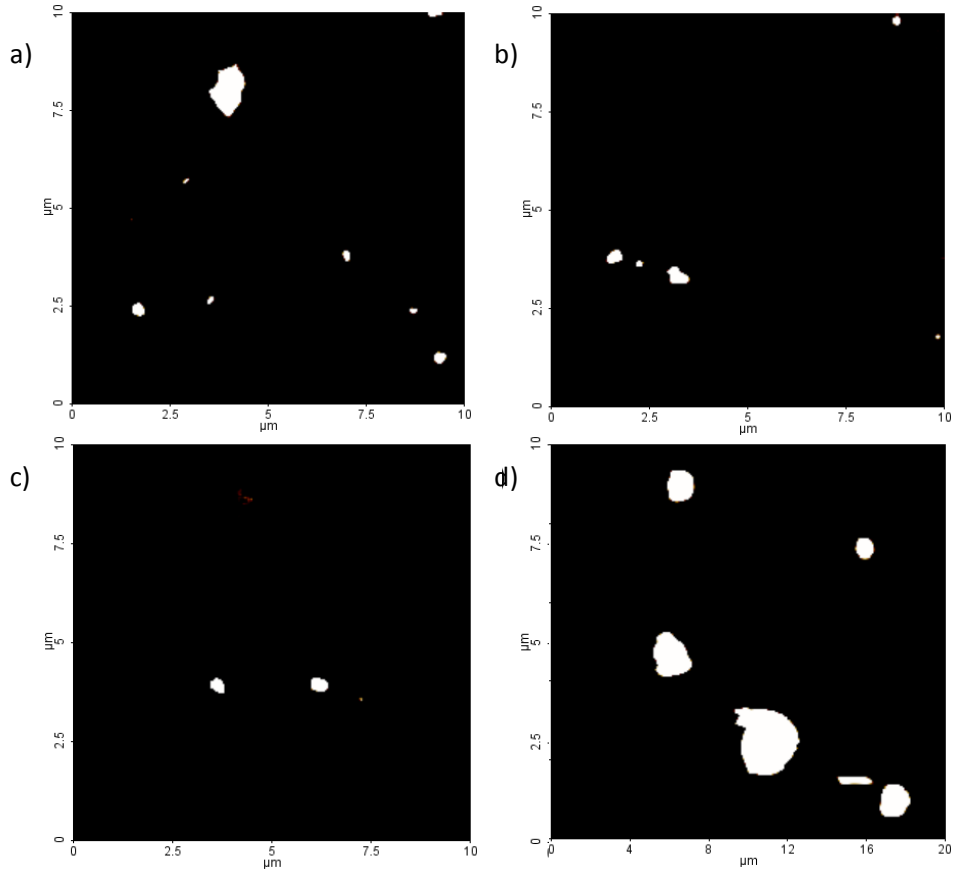


Figure 9.12 – Site 16 AFM images through treatment stages; a) Raw, b) clarified, c) filtered & d) post-GAC

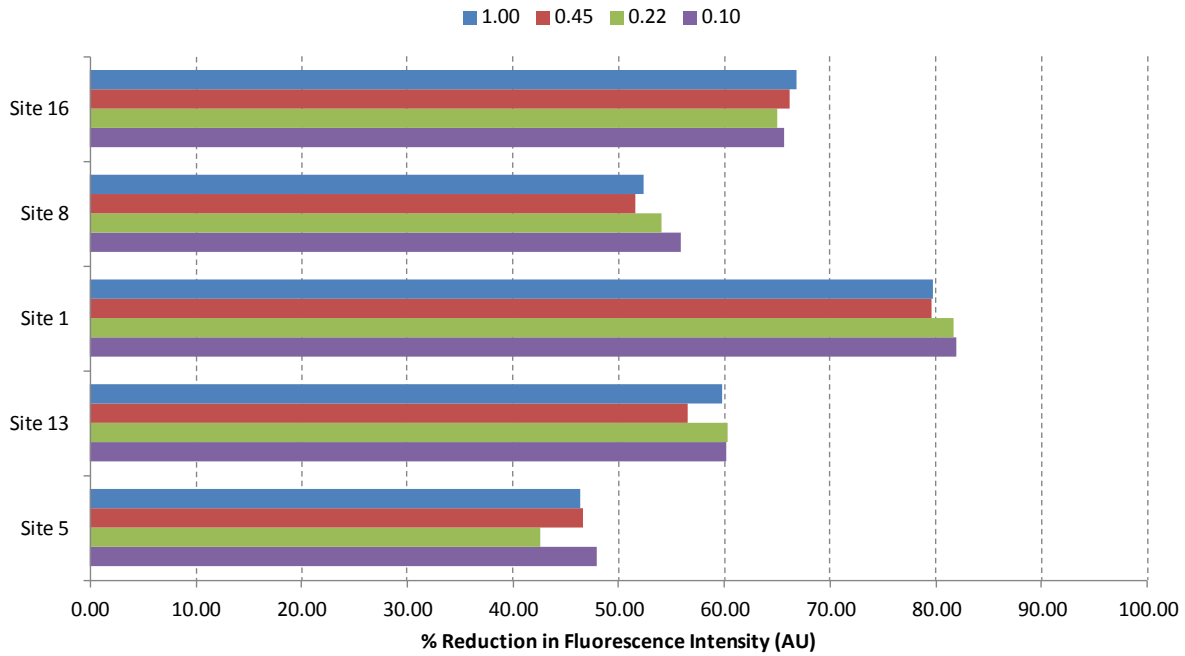


Figure 9.13 – Percentage reduction in fluorescence intensity in final waters

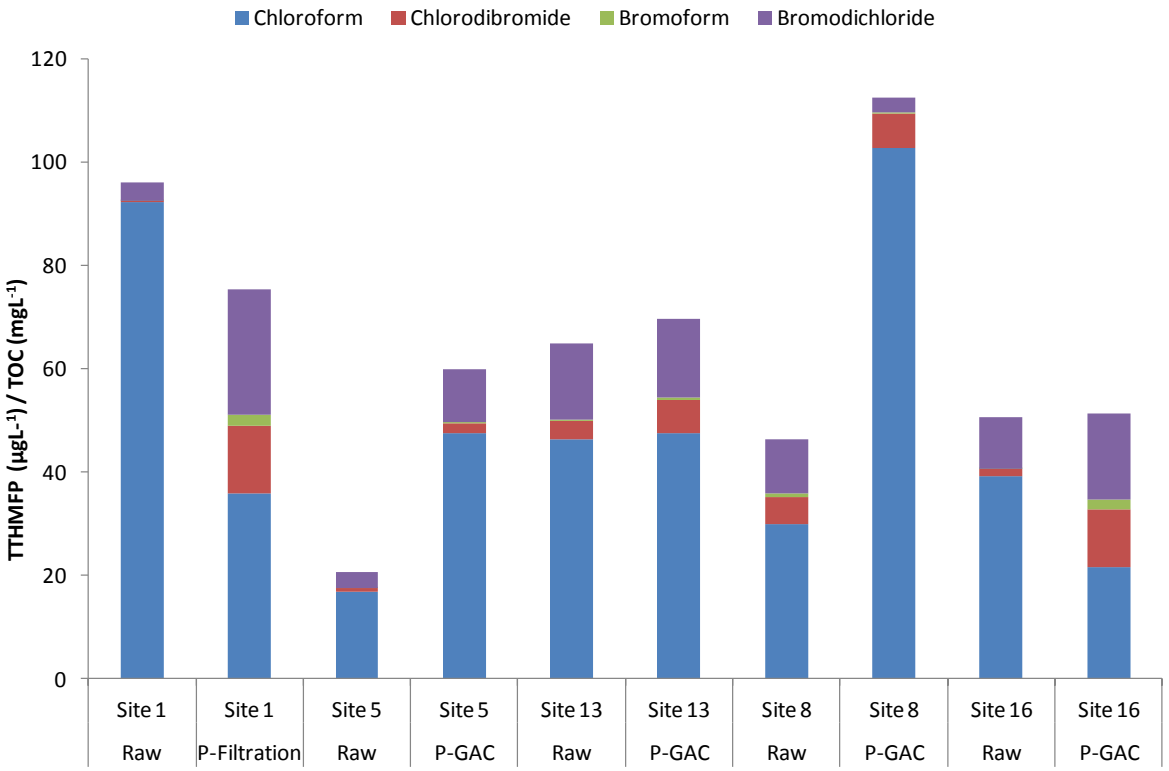


Figure 9.14 – TTHMFP/TOC for all sites

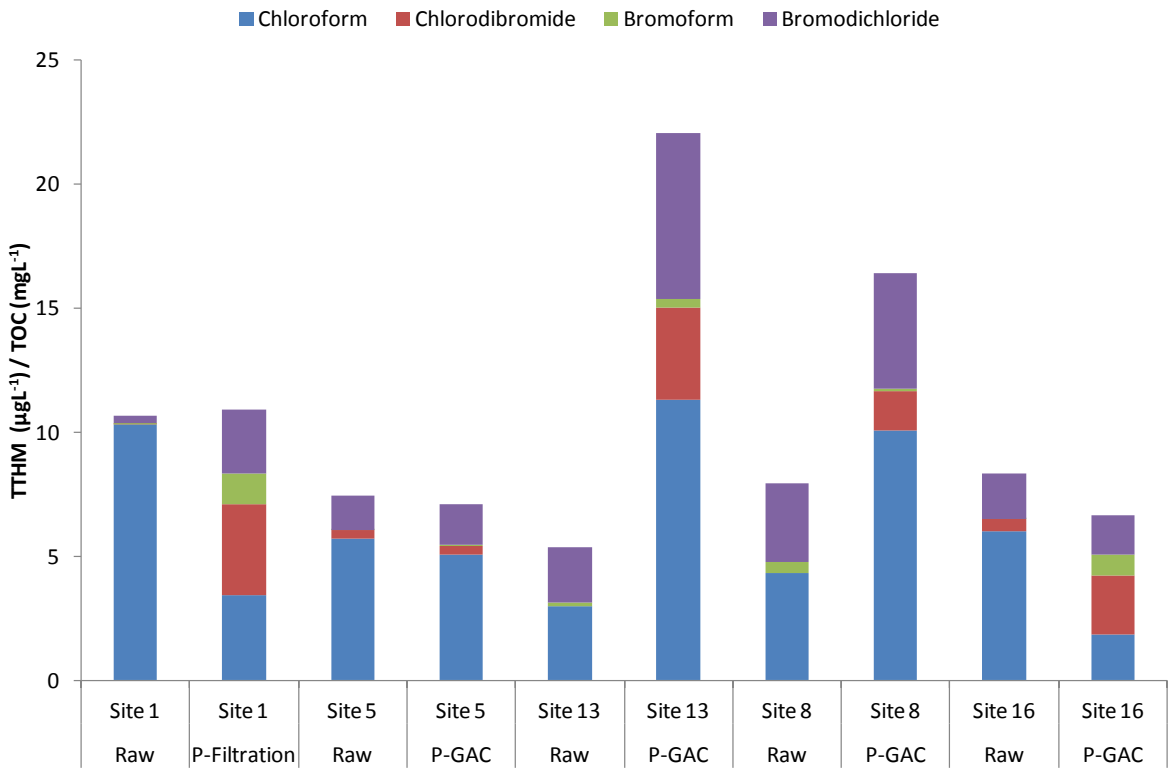


Figure 9.15 – TTHM/TOC for all sites

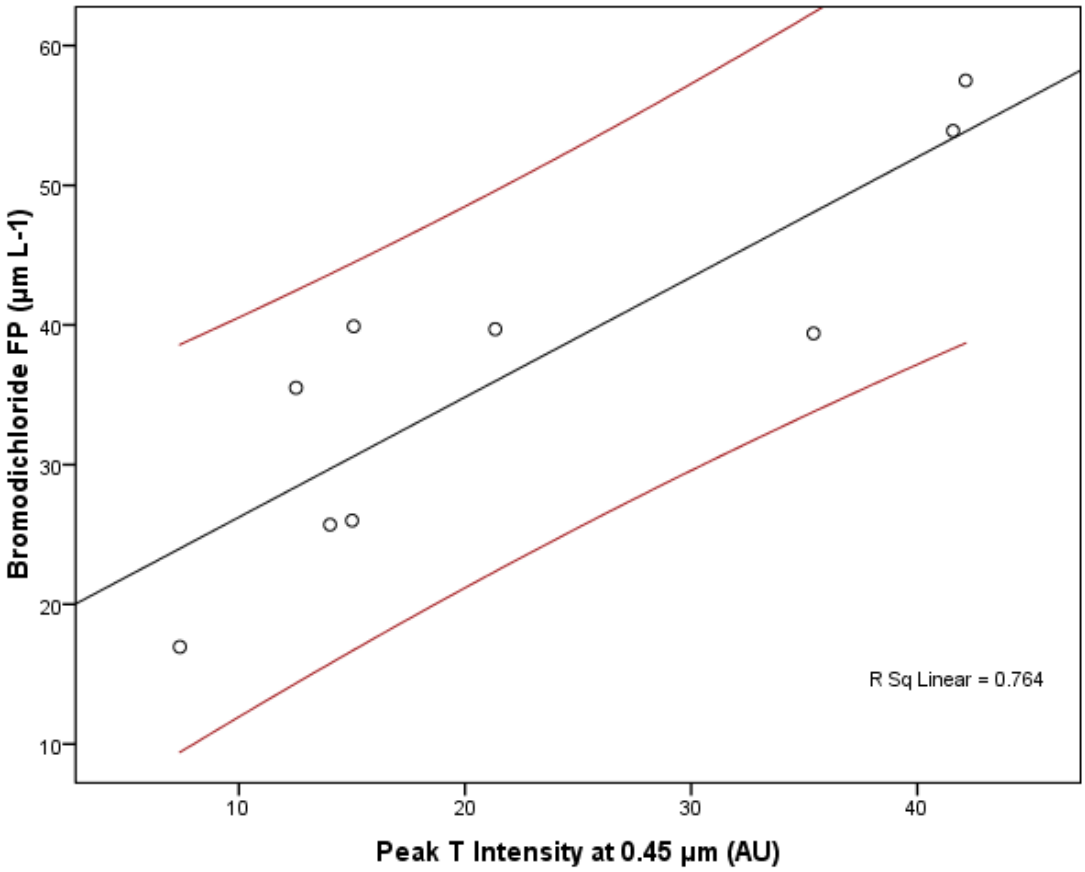


Figure 9.16 – Bromodichloride formation potential Vs Peak T intensity through 0.45 µm filter

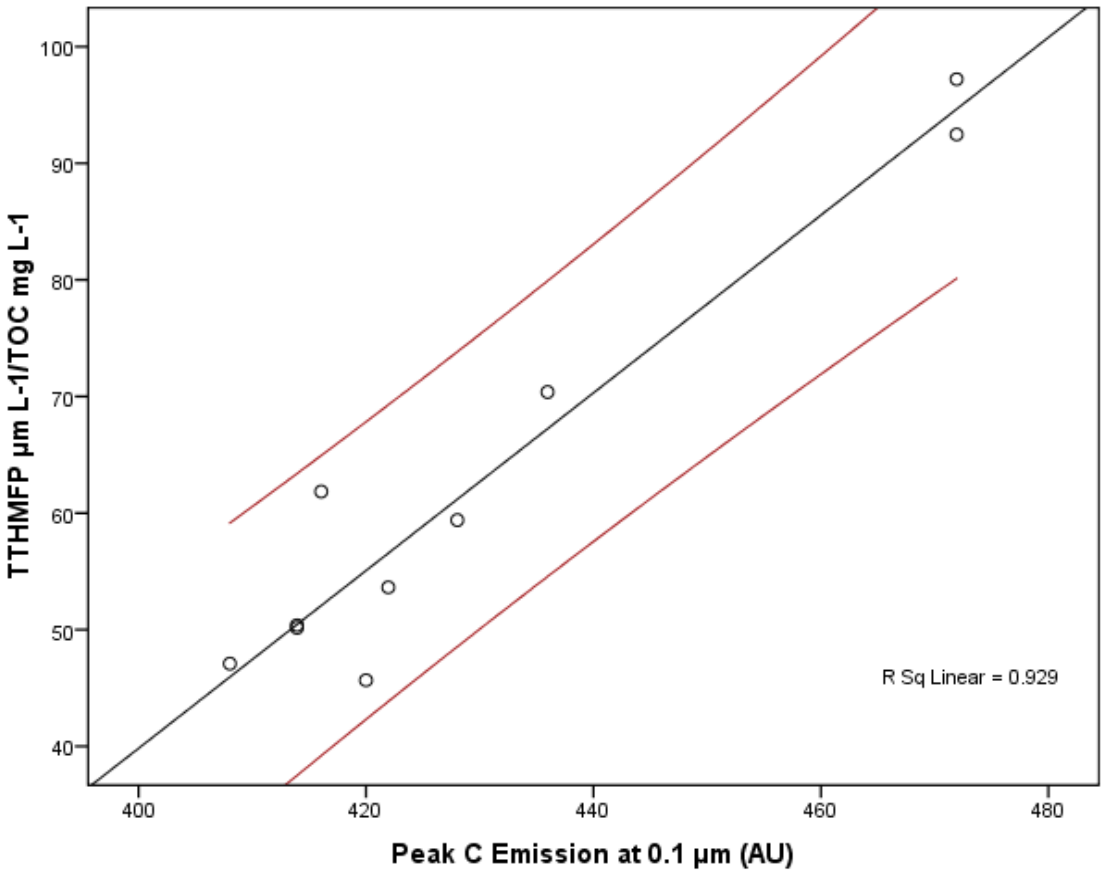


Figure 9.17 – TTHMFP/DOC Vs Peak C emission through 0.1 µm filter

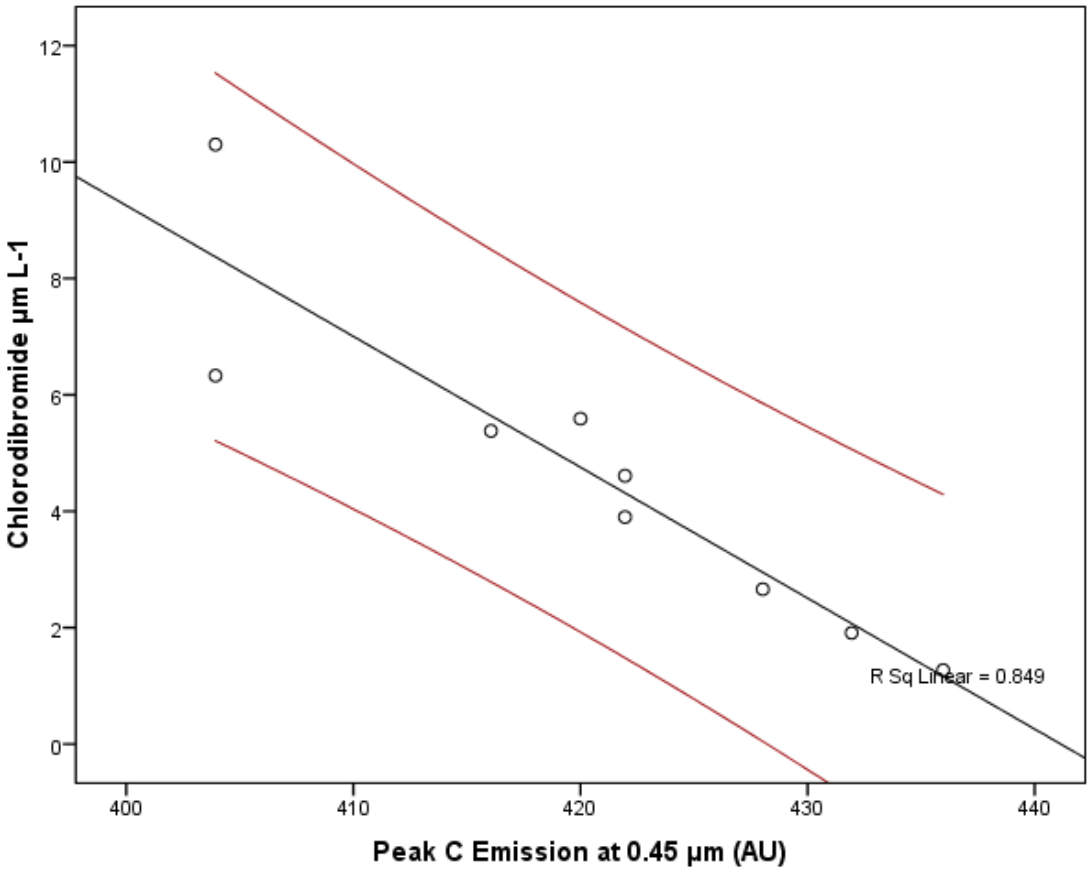


Figure 9.18 – Chlorodibromide Vs Peak C emission through 0.45 µm filter

Chapter 9 Tables

Table 9.1 – Raw water size fraction characteristics

Site	Size Fraction (µm)	UV_{254} (m^{-1})	Turbidity (NTU)	TOC (mgL^{-1})	Peak C Intensity (AU)	Peak T Intensity (AU)
Site 13	**<1.00**	0.57	0.24	3.9	143.22	47.95
Raw	**<0.45**	0.56	0.12	3.8	132.38	41.58
	<0.22	0.55	0.06	4.0	131.09	46.07
	<0.10	0.56	0.10	3.9	142.25	45.19
Site 5	**<1.00**	0.12	0.44	5.6	118.30	37.33
Raw	**<0.45**	0.12	0.13	5.7	113.00	42.14
	<0.22	0.12	0.08	5.6	112.49	42.59
	<0.10	0.19	0.07	5.5	115.65	40.06
Site 1	**<1.00**	0.42	0.47	7.1	151.96	13.98
Raw	**<0.45**	0.41	0.20	7.0	153.44	15.01
	<0.22	0.41	0.07	8.3	157.85	19.43
	<0.10	0.41	0.09	7.2	163.69	18.70
Site 8	**<1.00**	0.19	0.15	3.9	136.11	40.16
Raw	**<0.45**	0.12	0.07	3.8	137.69	35.41
	<0.22	0.11	0.06	4.0	144.51	40.53
	<0.10	0.11	0.06	3.9	141.74	37.38
Site 16	**<1.00**	0.17	1.94	5.6	174.95	50.58
Raw	**<0.45**	0.16	0.31	5.6	166.20	46.35
	<0.22	0.16	0.06	5.6	168.17	48.66
	<0.10	0.15	0.08	5.5	172.17	42.80

Table 9.2 – Raw water colloidal characteristics

Site	AFM Mean Particle size (nm)	Standard deviation (nm)	Particle Count	DLS Hydrodynamic Diameter (nm)	Standard deviation (nm)	Polydispersity index	NTA Hydrodynamic Diameter (nm)	Standard deviation (nm)	Conc. (per ml) $x10^8$
Site 13	28.8	7.6	70.0	387.0	83.0	0.6	196.0	94.0	1.0
Site 5	11.6	1.4	34.0	225.0	14.0	0.7	78.0	28.0	0.2
Site 1	65.2	27.2	6.0	150.0	31.0	0.4	111.0	43.0	1.7
Site 8	113.6	17.3	50.0	349.0	57.0	0.6	89.0	39.0	0.2
Site 16	110.6	35.5	34.0	365.0	41.0	0.5	92.0	60.0	2.5

Table 9.3 - Percentage TOC reduction through treatment

		Site 5		Site 13		Site 1		Site 8		Site 16	
		Individual	Cumulative	Individual	Cumulative	Individual	Cumulative	Individual	Cumulative	Individual	Cumulative
Clarification	1.00 µm	9.7		38.4		80.5		16.6		26.9	
	0.45 µm	14.7		36.0		82.0		19.1		27.0	
	0.22 µm	13.0		40.0		83.2		18.1		24.4	
	0.10 µm	8.0		36.7		79.7		17.1		24.1	
Filtration	1.00 µm	6.6	16.3	11.2	49.6	11.5	92.0	9.4	26.0	3.4	30.3
	0.45 µm	3.7	18.4	13.1	49.1	6.4	88.4	5.5	24.6	4.6	31.6
	0.22 µm	2.9	15.9	2.1	42.1	2.2	85.4	8.8	26.8	5.9	30.3
	0.10 µm	7.9	15.9	9.7	46.4	3.4	83.2	4.4	21.4	5.1	29.2
GAC	1.00 µm	18.8	35.1	17.2	66.8			18.9	44.9	42.1	72.5
	0.45 µm	20.3	38.7	10.8	59.9			20.2	44.8	40.6	72.2
	0.22 µm	20.9	36.8	24.6	66.7			19.5	46.4	40.6	70.9
	0.10 µm	18.4	34.2	23.8	70.2			18.6	40.0	39.6	68.8

Table 9.4 - Percentage reduction in organic fractions

Site	HPO (%)	HPIA (%)	HPINA (%)
Site 5	40.1	27.1	33.1
Site 1	91.0	26.2	52.9
Site 13	66.3	13.9	16.7
Site 8	42.5	28.1	41.7
Site 16	61.7	64.3	40.6

Table 9.5 – R^2 correlations for THMs with organics characterisation data

	Peak C Emission (AU)	Peak C Intensity (AU)	Peak T Intensity (AU)	TOC (mgL^{-1})
Chloroform-FP				0.45 µm, 0.83
Chlorodibromide-FP	0.22 µm, 0.82 0.10 µm, 0.76			
Bromoform-FP				
Bromodichloride-FP			1.00 µm, 0.82 0.45 µm, 0.87 0.22 µm, 0.79 0.10 µm, 0.84	
TTHMFP				0.45 µm, 0.86
TTHMFP/TOC	1.00 µm, 0.86 0.22 µm, 0.88 0.10 µm, 0.96			
Chloroform	0.22 µm, 0.77 0.10 µm, 0.77			
Chlorodibromide				
Bromoform				
Bromodichloride				
TTHM				
TTHM/TOC				

Table 9.6 – R^2 correlations between THMs and colloidal ICP-MS data

	Dissolved	Colloidal	Total
Chloroform-FP		Aluminium, 0.84 Chromium, 0.80 Iron, 0.95	Chromium, 0.78 Iron, 0.95
Chlorodibromide-FP		Calcium, 0.84	Antimony, 0.85
Bromoform-FP	Zinc, 0.85		
Bromodichloride-FP			
TTHMFP		Aluminium, 0.81 Chromium, 0.80 Iron, 0.95	Chromium, 0.80 Iron, 0.95
Chloroform		Aluminium, 0.91 Chromium, 0.82 Iron, 0.90	Chromium, 0.82 Iron, 0.90
Chlorodibromide			
Bromoform			
Bromodichloride			
TTHM		Aluminium, 0.80 Chromium, 0.77 Iron, 0.83	Chromium, 0.77 Iron, 0.83

Chapter 10. Discussion

In this chapter, results from the previous chapters will be discussed in relation to the relevant objectives.

Objective 1: To evaluate the use of existing characterisation methods for the investigation of NOM composition and in the identification of key trends in NOM character, existing and achievable removal and DBP formation.

Over a two year period, a detailed review of sixteen surface water WTW raw waters was undertaken. Monthly samples of raw and final waters were characterised using existing characterisation methods; UV_{254}, DOC, HPSEC, turbidity and SUVA. Quarterly, samples were investigated using THMFP, HAAFP and resin fractionations techniques in order to research the current and potential formation of DBPs through existing and low pH coagulation techniques and to further relate this to raw water composition. Current plant performance was evaluated with the use of DOC concentrations of final waters, and low pH jar tests performed at pH 4.5 simulated achievable DOC removals through the optimisation of existing practices. Due to the large number of sites in the investigation, three sites were chosen as a representative sample of the source water qualities for the region. Site 1 WTW was chosen for its high proportion of HPO NOM raw water, with Site 5 WTW having the highest proportion of low MW HPI NOM chosen for contrast. Site 13 WTW has an approximately equal mix of HPI and HPO NOM, but is also a direct river abstraction site where source water quality is known to change rapidly depending on current weather conditions.

Source water variations over the two year investigation period allowed for clear identification between the three chosen representative sites. Site 1 raw water predominantly consisted of high HPO content, accounting for 52 to 81% of total DOC. HPI content remained consistently low apart from the high intensity rainfall event in July 2007 where total HPI content increased to 40%. The widely reported autumn flush period (Chapman et al., 2008, Goslan et al., 2002, Sharp et al., 2006d) was also clearly evident in raw water fractionations with an increase in HPO content and overall DOC amount. In contrast, HPI NOM constituted the majority of total DOC in Site 5 raw waters. HPI content ranged from 45-74% over the investigation period. There was little variation between total DOC composition and concentration, apart from the high intensity rainfall event in July 2007. Site 13 WTW raw waters also remain fairly consistent, as with the relatively equal HPI/HPO composition split.

Existing NOM characterisation methods enabled a large scale investigation (16 sites) into NOM composition at Severn Trent Water sites; however the investigation also highlighted many positives and negatives of each method (table 10.1). Monthly samples consisted of UV_{254}, turbidity measurements, DOC, zeta potential and HPSEC. In the monthly samples, UV_{254} and fluorescence spectroscopy proved to be the greatest indicators of basic NOM character and removal potentials. For UV_{254} measurements, ease of use and application to predict DOC, SUVA and potentially THM formation (Her et al., 2008, Swietlik and Sikorska, 2006, Tipping et al., 2009) made it a very attractive possibility for fast and online NOM measurements. Experience of use and literature on UV_{254} does raise concerns however; UV measurements at a 254 nm wavelength exclude small aliphatic compounds that non light-

absorbing (Korshin et al., 2009) so NOM character and quantity can only be taken as an approximate value. Also, links to THM formation can be highly site-specific and it is worth nothing that in conventional treatment the larger HPO material were commonly associated with higher THM levels, but were also preferentially removed (Sharp et al., 2006d). Research on the use of UV in NOM characterisation is still being developed, in particular the use of a number of different wavelengths and linking UV to NOM reactivity (Korshin et al., 2009, Liu et al., 2010, Tipping et al., 2009). Current WTW standards are primarily driven by turbidity targets. This thesis demonstrates the potential for UV_{254} to be used for an indication of coagulant demand and residual organics in final waters, which could further enhance the use of UV monitoring in the water treatment industry.

Fluorescence spectroscopy analysis proved to be of most value in this investigation. The ease of use of the techniques, the rapid analysis and interpretation of results, and the close ties to TOC data meant that of all the techniques available, fluorescence would be most valuable on WTW (Henderson et al., 2009, Bieroza, 2009). The technique is still being developed however, and the main pitfalls of fluorescence spectroscopy lie within the analysis of results; identifying and analysing the areas of relevance. This could easily be overcome by dedicated software for specific emission and trend identification but a reliable online fluorescence device would need to be widely available first.

XAD resin fractionation provided a quantifiable measure of raw water polarity in terms of the HPI/HPO balance. Resin fractionation was only performed on quarterly samples as the separation technique as developed by Malcolm and McCarthy in 1992 is time-consuming and labour intensive on large numbers of samples (Malcolm and MacCarthy, 1992).

Research indicates XAD resin separation is used less frequently in characterisation studies due to the development of more rapid characterisation methods and concerns over the effect of pH changes on NOM composition and cross adsorption of fractions (Bond et al., 2010)but the research presented in this thesis showed that fractionation remains a definitive method of categorising absolute NOM character into its simplest terms (Kitis et al., 2002, Maurice et al., 2002, Schwede-Thomas et al., 2005).

HPSEC characterisation was again a method providing an insight into NOM composition, distinguishing by molecular size (Pelekani et al., 1999). In the thesis, HPSEC characterisation was used to successfully identify the molecular size ranges that were preferentially removed during treatment. HPSEC methods are again time consuming and expensive, and results processing is an extremely laborious process which also requires expensive computer software. Limitations of the technology were found to ultimately lie with the use of individual calibration techniques, making comparability of results between scientific investigations complicated (Wu et al., 2003). Peak fitting analysis provided a method of calculating peak areas, and therefore removal of individual molecular size ranges (Chow et al., 2008c). Peak fitting is a lengthy process however and would be unsuitable for large datasets or rapid analysis of results.

The strengths of HPSEC analysis were that it clarified the lower coagulation operating pH in chapter 6 was effective at removing a larger percentage of NOM across a wide range of MW (Budd et al., 2004, Gregor et al., 1997, Qin et al., 2006). It also verified that although there was substantial additional removal occurring at many of the typically problematic sites, there was limited removal of the low MW HPI NOM (Sharp et al., 2006a).

NOM characterisation methods were also used for investigations into DOC removal at the surface water WTW. As expected, current plant performance was highest at Site 1, the HPO dominant moorland site (Chow et al., 2008c, Sharp et al., 2006c). Site 5 waters exhibited the largest overall additional removal through initial low pH jar tests with an average current plant total DOC removal of 18.52% increased to 50-60%. XAD resin fractionation was used to show how months where the total HPI content was highest did experienced substantially reduced overall DOC removal, even in low pH jar tests shown in chapter 6. At the majority of sites, there was a clear distinction between the existing and low pH removal of DOC indicating that lowering coagulation pH altered coagulation charge mechanisms by promoting charge neutralisation to remove increased NOM (Cromphout et al., 2008, Jarvis et al., 2008). A comparison of actual NOM removal and source water characteristics using all characterisation methods concluded that even at sites with a dominance of HPI NOM, sites are commonly underperforming and have the potential to increase DOC removal substantially, and therefore reduce potential DBP production.

A review of scientific literature showed there were a vast number of studies into the characterisation of NOM, and many investigate links to DBP formation. Although the numbers of studies into NOM characterisation are relatively large, the major limiting factor is the spatial variance of NOM components. This essentially results in there being no one fixed definition of NOM character. This research was important as it demonstrates the benefit of NOM composition studies for WTW operation so there is a greater understanding of the limitations of existing treatment technologies and the potential to develop new treatment practices. The research presented in this thesis is also the first time such a large

scale study of a water treatment company's surface water NOM character and composition, and related this to treatment performance, compiled over a two year time period, capturing not only seasonal effects but also identifying the consequence of high intensity rainfall on NOM composition and character.

The formation of DBP is related to the incomplete removal of NOM during treatment processes reacting with disinfectants to form potentially carcinogeous by-products (Amy et al., 2000, Bond et al., 2010, Sirivedhin and Gray, 2005). Research also shows that DBP formation is also strongly dependant on disinfectant type, with chlorine disinfectants producing a greater array of DBP (Bull et al., 1995, Goslan et al., 2009, Hua and Reckhow, 2007) Initial characterisation investigations in chapter 4 reinforced the view that TTHMFP was influenced by the HPO content in surface waters (Jegatheesan et al., 2008, Wong et al., 2007). This led to an increased amount of TTHMFP at the moorland sites and HPO dominant sites (Goslan et al., 2002). TTHMFP analysis on final waters confirmed that as removal of HPO NOM was more consistent through treatment, the potential to form THM was significantly reduced. HPI dominated sites therefore had a higher potential to form potential carcinogeous DBPs, and would benefit from further investigation. HAAFP results showed similar formation patterns, however initial low pH coagulation experiments showed only small decreases in HAAFP could be achieved with optimisation.

Statistical analysis of characterisation data in chapter 5 allowed sites to be grouped into source water characteristics, and subsequently THM and HAA formation characteristics. Further investigations demonstrated links between NOM characteristics and individual THM, which could be employed on a site-by-site basis according to source water type.

Recent literature highlights relationships between THM formation and existing NOM characterisation methods (Chow et al., 2008b, Jegatheesan et al., 2008, Korshin et al., 2009). In these investigations, existing characterisation techniques provided a stronger basis for links between NOM character and DBP formation on a site by site basis. In all the analytical chapters, there were no clear links between characterisation techniques and DBP formation that could be used for DBP prediction at all sites. In future DBP investigations may need to be performed on sites grouped according to source water characteristics. It was also noted in chapter 6 that there were no clear links between DOC and actual THM formed in low pH jar tests at Site 13, a trend observed in similar studies (Brown et al., 2010)

The principal conclusions of this research are that existing treatment practices are inadequate for NOM removal and the reduction of potential DBP. Initial investigations on process optimisation infer that existing processes have the capacity to drastically improve NOM removal through low pH coagulation. The presence of low MW HPI NOM is however the major limit to existing coagulation methods so alternative treatment options would need to be considered if DBP formation increases or regulation limits decrease. Existing NOM characterisation methods were found to be inadequate at predicting the HPI content of NOM in surface waters, and many could be under-representing the HPI content of NOM and providing unreliable results. HPSEC and fluorescence spectroscopy represented the most capacity for accurate NOM characterisation.

Objective 2: To investigate the potential for carbon isotopic analysis and environmental colloidal analysis as NOM characterisation tools, to address current characterisation needs and to identify trends with DBP formation.

Due to the concerns over unrepresentative measurement of HPI NOM and limitations between links with DBP formation, NOM characterisation by means of carbon isotope analysis and environmental colloidal analysis was employed for the first time at three contrasting surface water sites.

Research presented in chapter 7 used carbon isotope analysis to characterise NOM at the three contrasting surface water sites but to also look at potential changes in NOM character through reservoir series. Samples were therefore taken from corresponding river, to WTW inlet. Carbon isotope analysis consisted of ^{14}C and ^{13}C signatures, in addition to a series of existing NOM characterisation methods. ^{14}C percentage modern results essentially determine the amount of pre-1950s material in the sample, from which a carbon age can be assigned. The higher the ^{14}C percentage modern, the younger the dominant material of the sample (Butman et al., 2007, Guo et al., 2009)g. ^{13}C signatures refer to the ratio of $^{12/13}C$ in a sample, which is ultimately determined by carbon fixation pathways. Carbon fixation pathways of plants in the northern hemisphere (C_3 plants) have ^{13}C signatures within an expected range. Derivations from this expected range could be due to an addition of carbon from an alternative source.

Carbon isotope results for Site 8 and Site 1 river samples had modern ^{14}C values and ^{13}C signatures within the expected C_3 plants range. A decline in ^{14}C percentage modern and shifts towards a heavier ^{13}C signature were only experienced in reservoir samples. This was observed at all three sites; however the largest variations were recorded at Site 8 reservoir systems. Comparisons with published literature on carbon isotope analysis of UK river

systems highlighted reservoir carbon isotope signatures were significantly different to those recorded (Sickman et al., 2010, Wei et al., 2010). Further analysis of relevant literature pointed to the occurrence of three potential scenarios;

- The leaching and transport of older organic material from catchments during low flow events (Tipping et al., 2010, Ziegler and Brisco, 2004);
- The preferential utilization of younger NOM by bacteria (Raymond and Bauer, 2001b);
- Destabilization of soil carbon stocks through climate change and intensification of agricultural processes (Austnes et al., 2010, Worrall and Burt, 2007).

These three scenarios could all account for a decreased percentage modern ^{14}C and/or a heavier ^{13}C signature, so carbon isotopic characterisation successfully demonstrated the changing composition of NOM in UK surface waters over relatively short time periods. Carbon isotopic analysis was then used to identify whether these trends had an adverse effect on water treatment processes.

In chapter 8, carbon isotope analysis of NOM character started with an initial investigation into post-GAC water at six surface WTW in 2008. Two separate sampling periods were employed to investigate seasonal impacts on carbon isotope signatures. When compared to carbon isotope signatures of UK river waters published in recent literature, ^{14}C signatures had lower percentage modern signatures but were within the range of reported literature. Contrasts between obtained results and literature were most evident in ^{13}C values, as $\delta^{13}C$ for the post-GAC samples were significantly heavier than previously recorded. Such results warranted further investigation to better understand the causes for the unexpected ^{13}C signatures.

In August 2009, further analysis was conducted at sites Site 8 and Site 16. Samples of raw, post-clarification, post-filtration, post-GAC and final water DOC were analysed, in addition to colloidal organic carbon from post-GAC and final waters. DOC samples for both sites remained within the expected range for C_3 carbon fixation pathway plants however variations were shown with colloidal organic carbon samples. Variations between dissolved and colloidal organic carbon were most extreme at Site 8 (-15.40‰ $\delta^{13}C$), although shifts towards an isotopically heavier ^{13}C signature in colloidal material were evident at Site 16 (-22.90‰ $\delta^{13}C$). Three potential explanations for the shift towards a heavier ^{13}C signature were then examined, with the use of literature to support arguments (Esteves et al., 2007, McCallister et al., 2004, Megens et al., 2002, Meier-Augenstein, 2010, Werth and Kuzyakov, 2010). The three potential explanations were;

- Fractionation of $\delta^{13}C$ during treatment;
- An inorganic/organic carbon interaction;
- An input during the treatment process.

It was concluded that chemical fractionation of $^{12/13}C$ during treatment processes, although likely, would not produce a large enough variation in order to account for the substantive shifts towards a heavier ^{13}C signature (Meier-Augenstein, 2010). An input from an inorganic/organic interaction was ruled out as water is not in contact with inorganic carbon for a sufficient enough time period and sample preparation techniques remove inorganic carbon from samples prior to analysis. It was therefore concluded that an addition of an alternate source of carbon from the GAC from either GAC fines or microbial growth could caused the unexpected results.

Comparisons with existing NOM characterisation techniques again gave little or no insight into the source or age of carbon. Turbidity, UV_{254} and TOC results all suggested the removal of NOM through treatment processes but gave no suggestion of an addition of carbon at any stage during treatment. This research was important as it was the first time carbon isotope analysis has been utilised in water treatment processes and it has led to increased understanding of the effect of water treatment on NOM. More importantly however, the research presented in this thesis has highlighted an inconsistency in NOM composition through treatment and identified an area in need of further investigation that would previously been left overlooked.

Colloidal and environmental nanoparticle analysis was also undertaken as it is an area where significant advances have been made in characterisation and consistency of analysis techniques of small scale materials. Colloidal and nanoparticle analysis was also considered due to the differing behaviour of colloidal material in surface waters (compared to particulate material) and increased reactivity as a result of larger surface areas (Baalousha and Lead, 2007, Matilainen et al., 2010) in the hope of identifying links with DBP formation and better characterisation of HPI material. Colloids and environmental nanoparticles are dominated by aggregation principals and are an important part of transport of contaminants in water systems (Gustafsson and Gschwend, 1997). Colloidal analysis of five STW surface WTW was then undertaken to characterise NOM and observe variations between sites. Sites Site 1, Site 8, Site 16, Site 5 and Site 13 were chosen and NOM characterisation was performed on material from four different size ranges; 1.00 µm, 0.45 µm, 0.22 µm and 0.10

µm. Colloidal and environmental nanoparticle analysis was performed on the 0.10 µm size fraction, consisting of AFM, NTA and DLS techniques.

At all five WTW, colloidal material (<0.10 µm) was highly polydisperse and prone to aggregation. NTA and AFM analysis provided information on particle sizes, with NTA recording the average particle sizes in the sample, whereas AFM refers to the smallest recorded particle size.

DLS analysis of NOM through the WTW showed the addition of coagulant significantly increased the aggregation potential at the HPO dominant sites Site 1 and Site 8. The lowest variation was shown at the HPI dominant sites Site 16 and Site 5. This clarifies earlier research which states that the HPI material is the least amenable to coagulation processes but that coagulation could also fail to destabilise the smaller particles, thus rendering them unlikely to form flocs and be removed out of suspension. Analysis of DLS results did however highlight that average particle size measurements were unrepresentative as some particles rapidly attached to one-another and the DLS software places a higher weighting to these larger particles. AFM and NTA analyses were able to give accurate mean particle sizes and smallest recorded particle sizes throughout the treatment processes, giving an insight into the behaviour and removal of the colloidal particle size range. AFM images were perhaps the most useful in determining the shape and size of particles and what effect, if any, were had on particles through treatment. AFM images showed water treatment processes destabilize particles, increasing their aggregation potential and altering colloidal shape, which could be a precursor for increased THM production. It is worth noting however that one significant problem that was encountered during this investigation was

that in many samples, the number of particles in the >0.1 µm range were very few, which hindered analysis.

DLS measurements also gave particle size data, however a limitation of the technology was that once a larger particle was recorded, this was awarded higher weightings and therefore influenced average partide results. As samples were polydisperse and prone to aggregation, DLS measurements were ultimately deemed unreliable. DLS did however give information of the aggregation potential of the colloidal material. Results showed that there was little to differentiate between sites and that this technique could be employed more effectively analysing colloidal material through the WTW process.

When comparing colloidal analysis with conventional characterisation techniques, this research has concluded that UV_{254} and turbidity measurements were not sensitive enough for analysis of size range characteristics after the initial raw water investigations. TOC measurements through treatment did however provide an invaluable insight into the preferential removal of size ranges at different works, and through each process. This research has highlighted areas for potential improvement and which processes were working most effectively. This could then be related back to NOM characteristics. When comparing colloidal characterisation methods to existing characterisation techniques, it was apparent that colloidal analysis gave little additional information on colloid character for the needs of this type of investigation.

Existing NOM characterisation methods used alongside carbon isotope analysis gave no indication of changes in NOM composition. Reductions in UV and turbidity were attributed

to settling of NOM in the reservoir itself. DOC measurements appeared to have no correlation with the stages of the reservoir system. Fluorescence measurements did however show correlations with carbon isotope signatures for ^{14}C and ^{13}C, with a R^2 of 0.75 and 0.65 respectively. These relationships were formed using small sample sizes, which would need to be taken into consideration when determining the robustness of algorithms.

The use of carbon isotope analysis in surface waters provided additional insight into NOM character and composition, one which existing characterisation methods are not designed to identify. This research was important as it highlighted the limitations of conventional characterisation methods and identified the benefits of carbon isotope analysis in NOM characterisation research.

New characterisation techniques carbon isotopes and environmental colloidal analysis did however fail to provide sufficient trends with DBP formation. A potential trend was identified between $\delta^{13}C$ and the coefficient of proportionality, K_{TC}, for potential formation of THM in isotopically heavier organic carbon. What was evident from the carbon isotope results however was that the type of NOM found in surface waters and the potential to form THM is not dependant on carbon age. Both studies did contain a limited number of data points in only one sampling period, so further investigation could be advantageous. Comparing DBP formation investigations throughout the analytical chapters, it becomes increasingly evident that DBP formation can only be predicted on a site-by-site basis, and for sites with an increased HPI content, there is still a significant knowledge gap for accurate analysis and prediction.

The use of carbon isotope and colloidal and environmental nanoparticle analysis techniques in water treatment is still a completely novel area of research. The knowledge obtained in this research will benefit the research community by testing techniques, and identifying the positives and negatives of each technique for use in NOM characterisation investigations.

Objective 3: To establish whether current treatment conditions are capable of removing increased amounts of NOM in order to reduce DBP formation.

Conventional mechanisms for the removal of NOM in water treatment include coagulation with metal salts (Edzwald, 1993, Rizzo et al., 2008, Sharp et al., 2006c). Coagulation involves a combination of charge neutralisation to destabilise outer particle surface charge to prompt successful collisions and adsorption onto hydroxide/precipitate surfaces (Gregor et al., 1997, Duan and Gregory, 2003, Yan, 2009). A number of alternative removal technologies are available, but many WTW are concentrating on the optimisation of existing practices through enhanced coagulation and process optimisation (Edzwald and Tobiason, 1999, Jarvis et al., 2008, Qin et al., 2006, Volk et al., 2000).

Low pH coagulation was employed at Site 13 WTW in order to quantify the effect of altering coagulation pH and dose on NOM removal and potential DBP formation. Three sampling periods were used in order to additionally observe NOM variation over the autumn flush period. Results showed that overall TOC removal was significantly dependant on source composition, with the lowest overall TOC removals occurring when HPI content was the highest. Lowering coagulation dose did have a considerable effect on overall removal however, and a reduction in coagulation dose at a lower pH did not adversely affect water

quality. Low pH jar tests confirmed that current works performance could be noticeably improved, which would have a positive impact on the reduction of DBP formation (Matilainen et al., 2010). Cost sheets and predicted THM and HAA formation were produced as a guideline for low pH coagulation, which could be developed for use on site for cost-benefit analysis.

HPSEC results for the investigation did highlight that even at a lower pH, the HPI NOM in source waters is unlikely to be removed through conventional coagulation and flocculation treatment alone and if DBP regulations reduce significantly then other treatment methods would need to be identified.

This area of research centred on the application of process optimisation research. This research was novel in the fact it applied low pH coagulation over a larger range of pH and coagulant doses and over an extended time period. It also demonstrated how DBP formation could be minimised by a low pH coagulation strategy and reduced coagulant costs. The benefit of the research to WTW is a basis for understanding how the NOM character impacts upon the success of low pH coagulation, TOC removal and DBP formation and what scenario would be most effective in practice.

Chapter 10 Tables

Table 10.1 – Review of NOM characterisation methods

Characterisation Method	Application	Positives	Negatives
DOC	Measure of total dissolved organic carbon in sample	Accurate, well-used process, can be used with UV_{254} to give indication of NOM composition, used as a measure of treatment performance and can be linked to DBP formation,	Just gives a measure of overall OM content of water
UV_{254}	A measure of the UV absorbing particles in a sample – linked to organic matter concentration	Used with DOC to give NOM composition indication, links with DBP formation and an indicator of coagulant demand and treatment performance, rapid measurement and on-line	May misrepresent the amount of OM in a sample as smaller HPI OM is not UV abosorbing, links to DBP formation may be site-specific
Turbidity	Measure of suspended solids in sample	A good measure of treatment performance and good for site use, rapid process and can be used for on-line measurements	In good treatment practices NTU should be very low, gives no indication of OM character or composition
XAD Resin fractionation	Method of separating HPO, HPIA and HPINA material	Identifies bulk quantities of OM fractions, correlates well with specific THM formation, good way of comparing OM composition between sites	Can be a lengthy process, the lowering of the pH to 2 could alter OM character, relevant literature has highlighted issues with
Zeta Potential	Measure of the outer surface charge of a	Good measure of optimal zone for	Optimal zone for DOC removal is only

	particle, used as an indicator for coagulant performance	coagulation removal by charge neutralisation and coagulation performance	very narrow and some variation was experienced. If pH control is not available on site then use will be limited.
$SUVA_{254}$	Used as an indicator of organic matter composition	Good measurement as if DOC is available then only a simple calculation is needed, quick measure of organic composition of sample	Research has questioned the limitations of SUVA as at 254 nm smaller chargeless particles do not absorb UV light therefore the reading would be unrepresentative of the total NOM in any given sample
HPSEC	A method of determining particle size ranges in a sample	Gives a detailed view of composition and size range of OM in a sample	Requires peak-fitting software to analyse samples accurately, lab based procedure that can take time to perform, issues over column type, adsorption and calibration
Fluorescence	A measure of humic-like, fulvic-like and protein-like material in a sample	A rapid measurement tool that can accurately predict the type and amount of OM in a sample	Still being developed, relatively new to the industry and would need specific equipment to be designed as well as analysis software
Carbon isotopic analysis	A measure of carbon age and source	Gives carbon source and age information which none of the other analysis procedures are able to provide	Lengthy analysis procedure that is complicated to perform and very expensive per sample
DLS	A measure of particle size, diameter and aggregation potential	Quick and simple to use, and uses software and hardware that is already available (zeta potential software)	If samples are polydisperse, can give unrepresentative reading of average particle size, provided no link to DBP formation

NTA	A measure of particle size and particle size range	Sensitive technique providing detailed particle size information	Lab-based analysis which would require specialist training to perform, gave no link to DBP formation, limited current use in water treatment and NOM characterisation
AFM	A measure of particle size, shape and a sensitive imaging technique	Sensitive technique providing detailed particle size and shape information	Lab-based analysis which would require specialist training to perform, gave no link to DBP formation, limited current use in water treatment and NOM characterisation

Chapter 11. Conclusions

11.1 Conclusions

- This is the first time a large-scale review of coagulation practices at all of Severn Trent Waters' sixteen surface water treatment works has been conducted. Research indicated current coagulation conditions are unsuitable for optimal removal of NOM and subsequent DBP precursors.
- A large-scale review of existing and new NOM characterisation methods was performed and determined that existing methods are unable to accurately predict the HPI content of NOM, and therefore provide confident links to DBP formation potential.
- Seasonal variations in NOM character and composition are more prevalent at HPO-rich upland sites, whereas lowland HPI-rich are less susceptible to seasonal variations.
- With the use of statistical analysis techniques it is possible to split the Severn Trent surface water sites into three distinct types, dependant on raw water quality. These three types of raw water profile give information on source water quality, expected and achievable removal rates of NOM and the potential formation of THM, THMFP and HAAFP.
- Type 1 raw waters are typically moorland source waters with a dominance of HPO material. Type 1 waters show distinct seasonal variations, with late summer and autumn periods experiencing notably higher total DOC concentrations and HPO

content. Regression relationships indicate a correlation between chloroform and HPO in Type 1 waters. Months with increased quantities of HPO were found to have higher chloroform formation occurring after treatment, indicating that HPO is typically a precursor for chloroform at these sites.

- Type 2 raw waters contain a mixture of both HPO and HPI material, with minimal seasonal shifts. THM precursor relationships were identified by notable correlation between the potential formation of bromoform and HPINA.
- Type 3 raw waters characteristically consist of low molecular weight, HPI NOM. Principal component analysis identified seasonal trends with reduced UV, DOC and peak C intensity in spring and summer months. Strong relationships between potential THM chlorodibromide and bromoform were observed with HPO and HPI NOM respectively.
- The use of carbon isotope analysis through the water treatment process is entirely novel research employed to gain further insight into the selective removal of NOM components. Through this investigation it was identified that treatment processes targeted the removal of older NOM in coagulation and GAC whereas filtration and chlorine disinfection targeted younger NOM, reducing the percentage modern ^{14}C.
- Post-GAC colloidal NOM had heavier ^{13}C signatures and a decreased percentage modern carbon ^{14}C. Explanations for this point to the addition of GAC fines, fractionation of $^{12/13}C$ through treatment processes or through microbial growth on the GAC column.
- The use of carbon isotopes for NOM characterisation was found to provide an insight into NOM age and composition through reservoir systems and water treatment processes that existing methods were unable to provide.

- Reservoir storage leads to an isotopically heavier ^{13}C signature and a decreased percentage modern ^{14}C. Possible explanations for this included the leaching of older carbon from lower down the soil profile within catchments, the preferential utilisation of younger NOM in bacterial processes and an increase in carbon in surface waters through the destabilisation of soil stocks through intensified agricultural processes.
- The use of colloidal and environmental nanoparticle imaging techniques was employed as a novel NOM characterisation method through water treatment. AFM and NTA techniques were used to measure changes in colloid size and shape. AFM images also showed the destabilization of particles through the treatment process. DLS measurements were found to be unrepresentative of colloid size compared to AFM techniques, however were used to measure colloid polydispersity.
- For the use aims of this investigation, it was determined colloidal and environmental analysis would be unsuitable for NOM characterisation.
- For DBP precursor removal by conventional methods, initial low pH coagulation tests on all sixteen surface water treatment sites indicated NOM removal increased to a minimum of 50-60% removal at all sites, even at sites with a 10-30% average removal. Up to 90% removal of NOM was also observed at HPO-rich moorland sites.
- A more detailed low pH coagulation investigation was undertaken at a direct river abstraction Type 2 site. The most significant removal of NOM was observed when coagulation was performed at pH 4 and 4.5 however, any small reduction on pH proved to have a positive impact on NOM removal.

- The removal of HPI NOM was found to be minimal even in low pH conditions and has been identified as an area where research into additional removal methods or alternative coagulants needs to be focused.

11.2 Future work

- This thesis has highlighted a need for further investigation into HPI characterisation methods and the need to identify a method that can provide robust correlations with DBP formation.
- There is also a need to develop a robust system for NOM characterisation and DBP formation for online use at WTW.
- Using existing methods of NOM characterisation and links to DBP formation, assessments for potential DBP formation would need to be produced on a site-by-site basis.
- NOM characterisation results could be used to influence treatment strategies at WTW, to identify WTW where improvements to NOM removal could be made with conventional treatment, and the identification of sites where additional removal technologies need to be considered.
- Fluorescence spectroscopy is proving to be a highly valuable and versatile technology, and could provide a wealth of information for WTW operation if employed correctly. Further research would need to be on developing a results interpretation programme and online monitoring systems.
- Carbon analysis highlighted a potential input of carbon into the WTW, this area would benefit from further analysis to investigate an input of carbon, and subsequent mitigation in water treatment. Limitations with the technology lie with cost and time, so the use of ^{13}C alone (as it a significantly quicker procedure) would be better employed in future studies.

- The impact of increasing carbon levels in surface waters would also need to be investigated further as this could have a significant impact on water treatment in the future, and subsequent DBP formation levels – placing further strain on WTW especially if regulation limits become tighter.
- Future research would benefit from a large scale analysis of carbon isotopes in surface waters on the various size ratios of NOM in order to determine the impact of NOM size and settling on carbon isotope signatures.
- Current removal of NOM through coagulation is insufficient if regulations on DBP formation were to be lowered. WTW would benefit from individual site recommendations on operating procedures and investigations into increased NOM removal – through low pH coagulation or process optimisation.
- Low pH coagulation cost analysis and DBP formation figures could be used to create a strategy for increased TOC removal and specific works, and low pH coagulation DBP formation matrix could be used in conjunction with previous Severn Trent research into DBP formation through distribution systems.

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